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EDITORIALS.

ANTIQUATED CUSTOMS.

THE timidity of capitalists and manufacturers is proverbial. When this timidity is coupled with the idea that a certain practice is profitable, the normal wise conservatism of practical men degenerates into the fetich worship of obsolete customs. The common alkalis depend for their usefulness in chemical manufacture upon their alkalinity—there is little possibility of a chemical argument about that point. The determination of the value of a given shipment of alkalis would naturally involve an alkalimetric analysis and a calculation to the result to Na_2O (the trade custom), NaOH or Na_2CO_3 , as the case might be. It is customary to base the price of alkalis upon "60° alkali" which means a hypothetical alkali containing 60 per cent. Na_2O . The price is then adjusted according to the analysis. In the purchase of caustic soda, no allowance is made for the small amount (2-4 per cent.) of sodium carbonate always present. These points, however, are not of the greatest importance in this connection. Instead of using the rational method of calculating the percentage of Na_2O present by using the factor 31 ($\text{Na}_2\text{O} = 62; 62/2 = 31$), derived from the atomic weights of the elements, it is customary in the trade to use methods of calculation which are known as the "English," "Newcastle," or "Liverpool" "tests." Pure sodium carbonate contains the equivalent of

58.49 per cent. Na_2O thus: $\frac{31 \times 100}{53} = 58.49$ per cent. According to the "Newcastle" "test," however, it would contain 59.26 per cent. thus: $\frac{32 \times 100}{54} =$

59.26 per cent. According to the "Liverpool" "test," the figure is higher yet, since the factor 32 is arbitrarily used in place of 31. The calculation is: $\frac{58.49 \times 32}{31} = 60.37$ per cent. Therefore, according

to the Liverpool test, pure sodium carbonate would contain 60.37 per cent. Na_2O , instead of 58.49 as demanded by theory! This amounts to an increase of 3 per cent. in round number. This practice is hoary with age, venerable and venerated by the soda trade. Manufacturers and middlemen look upon it in the light of gospel and revelation. The chemical trade is full of such customs, which have grown flat and stale but not necessarily unprofitable. Another example is the so-called "refraction test" or "West Coast method" which is applied to the analysis of commercial sodium nitrate, which is largely imported from Chile for use in the manufacture of nitric acid, explosives and fertilizers. The valuable constituent in this chemical is nitrate nitrogen, and this can easily be determined by one of several good methods—possibly best by Lunge's nitrometer, or the Schloessing-Wagner method. In the trade, however, no direct determination of nitrate nitrogen is recognized. Instead the "refraction test"—save the name!—is applied. The refraction test consists in determining moisture, insoluble matter, sodium sulphate (calculated from SO_4), sodium chloride (calculated from Cl) and subtracting the sum of these from 100 per cent. Naturally the result shows more nitrate of soda than is actually present. There is no excuse for the continuance of obsolete trade customs such as these. They are thoroughly unscientific and misleading. It would probably be urged by the producers and middlemen that as prices are based on analyses and calculations made according to these so-called "tests," it would upset the trade to change the custom. As a matter of fact the price readjustment could be made overnight, and afterwards would take care of itself. In matters of this sort (and we have mentioned but two of a large number of bad trade customs) the conservatism of trade is almost if not quite identical with the inertia of stupidity.

THE PHOSPHORUS MATCH.

WILLIAM H. TAFT, President of the United States, in his Message to Congress of December 6, 1910, wrote in regard to the phosphorus match industry:

I invite attention to the very serious injury caused to all those who are engaged in the manufacture of phosphorus matches. The diseases incident to this are frightful, and as matches can be made from other materials entirely innocuous, I believe that the injurious manufacture could be discouraged and ought to be discouraged by the imposition of a heavy federal tax. I recommend the adoption of this method of stamping out a very serious abuse.

A leading daily newspaper commented editorially as follows on this part of the President's message:

In nearly every civilized country except the United States, the use of white phosphorus in the making of matches is prohibited by law. The cost of production is increased only about 5 per cent. by the adoption of substitutes for white phosphorus, but because of competitive conditions one manufacturer cannot adopt the safer and more expensive method unless all will do the same. The leading manufacturers of matches in this country, it is said, would welcome any legislation that will put an end to the use of white phosphorus in their industry.

Legislation in harmony with this wise recommendation ought to be enacted at the present session of congress. The imposition of a prohibitive federal tax on the manufacture and sale of matches containing white phosphorus would constitute the best method of dealing with the problem.

On the editorial page of another prominent daily newspaper appeared the following:

It is hoped that the present session of congress, short as it is to be, will see the passage of Representative Esch's bill directed against poisonous matches. President Taft has again taken sufficient interest in the subject to mention the necessity of legislation relating to it in his message. The American Federation of Labor and other bodies are interested in the abolition of the poisonous match for the sake of the match workers who are constantly exposed to the deadly phosphorus fumes.

Matches made with the only known substitute for white phosphorus are controlled by a patent held now by the match trust. This patent will expire in five years, but in the meanwhile the terms on which the trust allows it to be used by independent manufacturers are such that the latter have not generally taken advantage of them. And in the meanwhile five years remain for the workers to be exposed to the poison. The trust demands \$100,000 for the rights remaining its property. If our chemists cannot discover another process by which to make matches at once good and safe, it would be worth that sum to save the workmen from five years of danger.

Distasteful as a prohibitive tax on matches would be, it seems the only remedy in the circumstances. This country is a whole generation behind Europe in the regulation of this dangerous trade. It should either be made safe or be taxed out of existence.

Throughout the country the newspapers have generally given voice to their ideas in similar outspoken tones. The universal attitude in the matter appears to be that the United States government has been negligent in failing to protect the workers in the yellow phosphorus match industry. At the same time the plea is made that this protection be no longer withheld and that the Esch bill be passed. American matches have not enjoyed the highest reputation possible in the past. Mr. Carl Baedeker, careful observer of international conditions for the benefit of the traveler, says in "The United States: Handbook for Travellers:" "The prices of many manufactured goods are much higher in the United States than in Europe; and the traveler should, therefore, come provided with an ample supply of all the articles of personal use he is likely to require, down to such small items as, and matches (often very poor in America)." This merely in passing.

During the year 1910, the Bureau of Labor issued a monograph from the pen of Dr. John B. Andrews, entitled "Phosphorus Poisoning in the Match Industry in the United States." This was published

in Bulletin 86 of the Bureau of Labor, and was undoubtedly the occasion for the paragraph in President Taft's Message quoted above. Dr. Andrews' report was based on the results of a careful investigation into the working conditions in 15 out of the 16 factories operating in the United States. During the preliminary investigation, 16 cases of phosphorus necrosis were discovered in the factories and when the investigators, in an intensive study of three factories, directed their attention to the homes of the workers, a total of 82 cases was discovered in the homes of the workers in these three factories. It was ascertained that at least eight perfectly developed cases occurred in two factories during 1909. According to the report, 65 per cent. of the workers in the 15 factories investigated were working under conditions which exposed them to phosphorus fumes, and the women and children were much more exposed than the men, the figures being 95 and 83 per cent. respectfully. In the 15 factories 3591 employees were at work. Of these 2024 were men, 1253 were women and 314 children under 16 years of age. In a number of the factories, ventilating and general sanitary arrangements, such as washing facilities and eating places, were found to be far from satisfactory.

Exposure to the fumes of phosphorus gives rise to two forms of poisoning. The first is rare and is a mild chronic form characterized by cachexia, jaundice, anemia and albuminuria. In more advanced cases there may be chronic enteritis, diarrhea, bronchitis and even a peculiar fragility of the bones. The ordinary form or phosphorus necrosis gives rise to periostitis and necrosis of the lower jaw. It usually begins, though not necessarily, from a decayed tooth or a lesion of the gum. The teeth become loose and drop out, the jaw becomes swollen and painful, and discharges large quantities of pus together with pieces of dead bone. The removal of the entire lower jaw is often necessary to stop the course of the disease. Death frequently results. This form of poisoning is known to the workers in match factories as "phossy jaw." It is the element phosphorus itself, and not its compounds, which produces the symptoms. It has been found in the blood as such. Its oxygen acids are without poisonous effect. Practically all cases of phosphorus poisoning have been due to white (yellow) phosphorus, since this is more volatile and more soluble than the red variety. Phosphorus sesquisulphide, P_4S_3 , which is used in the French government match factories, appears to be even safer than red phosphorus, for the small amounts of phosphorus released from it in the tissues are too small to induce symptoms. In tabular form a brief statement of the history of the development of chemical and friction matches would appear as follows:

- 1669 Brand (Hamburg) discovered phosphorus.
- 1771 Scheele prepared phosphorus from bone ash.
- 1812 Sulphur matches tipped with $KClO_3$ and sugar.
Ignited by H_2SO_4 .
- 1816 Derosne made phosphorus mass for matches.

- 1827 Friction matches (England) Sb_2S_3 and KClO_3 .
- 1837 Substitution of PbO_2 and $\text{Pb}(\text{NO}_3)_2$ for KClO_3 in phosphorus match.
- 1845 Schrötter (Vienna) discovered and identified red phosphorus.
- 1848 Böttger invented "safety match" containing no phosphorus, and striking on red-phosphorus-coated striking surface.
- 1858 Lundström manufactured safety matches in Jönköping (Sweden).
- 1897 France prohibited use and manufacture of yellow phosphorus match.
- 1903 Germany prohibited yellow phosphorus match. Law effective Jan. 1, 1907.
- 1906 Berne treaty. Prohibition of yellow phosphorus match in France, Denmark, Luxembourg, Italy, Switzerland, Netherlands, Germany.
- 1908 Great Britain prohibited yellow phosphorus match. Law effective Jan. 1, 1910.

At the present time there are three principal kinds of matches manufactured. First the "safety" match containing no phosphorus and designed to be struck on a prepared surface containing red phosphorus. A characteristic composition for match heads of this sort contains potassium chlorate, potassium bichromate, sulphur, manganese dioxide, iron oxide, glass powder, glue and gum arabic. The striking-surface composition contains red phosphorus, antimony trisulphide, dextrin, and lampblack. The second kind of match is the ordinary "strike-anywhere" or parlor match, containing yellow phosphorus and designed to light when rubbed against any rough surface. A characteristic composition contains glue, glass powder, iron oxide, lead oxide, and phosphorus. The principal variety of this kind of match is that which lights only when rubbed on the tip, not on the side. The third kind of match strikes anywhere but contains no elementary phosphorus. The most successful match of this sort heretofore has been that whose composition contained phosphorus sesquisulphide, P_4S_3 . It is stated that 3.5 g. of this substance, corresponding to 6000 matches, shows no harmful action. The French government match factories, following the procedure of Sévène and Cahen, use phosphorus sesquisulphide in formulas containing also potassium chlorate, zinc oxide, ochre, glass powder, and glue. Various other substitutes for yellow phosphorus in "strike-anywhere" matches have been suggested and tried, with more or less success, in an endeavor to discover a better substance for the purpose than phosphorus sesquisulphide. The latter has the disadvantage of decomposing when stored for some time in a damp place, giving rise to the offensive hydrogen sulphide gas. The list includes a mixture of phosphorus trisulphide and pentasulphide or triphosphorus hexasulphide, zinc thiophosphite, bright-red phosphorus (Schenk), phosphorus suboxide and cupro-barium polythionate. The list will no doubt be extended in the near future, and an entirely unobjectionable substance found.

As many as five years ago matches were manu-

factured and distributed in the United States containing no poisonous phosphorus, thus demonstrating the practicability of the process. Each box bore the legend: "These matches do not contain phosphorus. A new discovery." They were found upon experiment to strike perfectly on suitable rough surfaces such as wood and cloth and ordinary objects.

The following statements are quoted verbatim from Dr. Andrews' report:

Those who have followed the results of studies of the conditions surrounding industrial employments with reference to the effect upon the health of the employees are impressed by the possibilities of a scientific movement to improve working conditions and reduce occupational dangers. The manufacture of matches in the United States beyond any other industry presents an opportunity to improve conditions and easily to make a most dangerous industry entirely harmless. Peculiar to this industry is a disease which, without great expense, without a long struggle against poverty, indifference, ignorance, and neglect, may be absolutely eliminated by the prohibition of the use of white phosphorus. This disease, known to medical and dental professions as phosphorus necrosis, continually threatens those who work in match factories where poisonous phosphorus is used. The phosphorus most frequently attacks the jaw bones, and sometimes necessitates the removal of an entire jaw by surgical operation. A harmless substitute for the poison that is commercially practicable is readily available. Why, then, do our manufacturers not use this substitute? Many would gladly do so, but it costs just a little more to make nonpoisonous matches. Condition is so keen that a single manufacturer can not place himself at natural disadvantage with his rivals in business.

In the leading countries of Europe the governments have come to the aid of both workers and manufacturers by requiring all manufacturers to discontinue the use of the poison. In these countries the manufacturers are all on an equal footing in competition and the danger of phosphorus poisoning is entirely eliminated.

And again further on:

The company owning the patent rights for the use of sesquisulphide of phosphorus in the manufacture of matches in America believing this article to be a remedy for the prevailing trouble in manufacturing matches, namely phosphorus necrosis, has expressed (in writing) its willingness to permit the use of the sesquisulphide of phosphorus by other manufacturers on equal terms, if the use of white phosphorus is prohibited by law.

It would seem that the time has come when the government must take definite and positive action which will lead to the prohibition of the poisonous phosphorus match. Regulation will not suffice. Prohibition is necessary. If President Taft's recommendation for a prohibitive tax is the best form for the legislation to take, the needed law should be passed without delay.

THE PRICE OF GLYCERINE.

CRUDE, C. P. and dynamite glycerine have commanded high prices during the year 1910. During the latter part of the year C. P. glycerine was selling for 24½¢. per pound in drums, the price not including the package. In early November, soap lye crude glycerine reached the astonishing price of 17¢. per pound, basis of 80 per cent., and saponification crude sold proportionally higher. The causes of these high prices have been variously stated by different observers. Among the explanations advanced are the following: the prevailing high prices of all commodities; the high prices commanded by fats and fatty oils; the great demand for explosives for construction work on the Panama canal; general activity

in construction and mining requiring the use of explosives. Whatever the immediate cause, undoubtedly the demand for glycerine to be used in the manufacture of nitroglycerine explosives is the determining factor. The United States is a great producer and consumer of glycerine. In spite of the fact that this country produces enormous quantities of glycerine in soap and candle factories, very large quantities of crude and refined glycerine are imported from all parts of the world. A considerable part of the glycerine imported from foreign countries is probably derived from fats and oils originally exported from the United States. At the same time, Australia, Argentina and Russia are large producers of animal fats, and tropical oils are entering the European market in constantly increasing volume. At present prices, when glycerine sells for two or three times the price of the raw material from which it is derived, it must be considered as something more than a by-product—it becomes one of the principal products of the saponification of fats, even in the commercial sense. The amount of glycerine left behind in soap, and not won from fats in the autoclave becomes of greater relative importance. Of the total glycerol theoretically yielded by fats (about 10.6 per cent. for neutral tallow), good soap factory practice will recover from 80 to 90 per cent. and of this the still will win 97 per cent. or more. These are good yields and the percentages in many factories will not run so high. In the autoclave, 95 per cent. can usually be recovered. Nevertheless there appears to be an opportunity here to improve the practice in such a way, that to the future chemist, present-day yields will appear low and present-day practice wasteful. For some months, the soap-factory chemist has been watching the soap kettle closely to obtain greater yields and studying methods to reduce the percentage of glycerol in cold-made soap (of no apparent use there); and beyond a doubt the soap factories all over the world are obtaining higher yields of glycerol to-day than they were two years ago. Thus may the enhanced value of a product stimulate chemical control to the point of developing improved practice without any new discoveries or innovations in manufacture.

ORIGINAL PAPERS.

WASTE WOOD AND ITS UTILIZATION.

By GEORGE B. FRANKFORTER.

The United States is the most wasteful nation in the world: wasteful in living, wasteful in manufacturing, and wasteful in conserving its natural resources. This prodigality of the nation's wealth has been largely due to extravagant methods of manufacture. A quarter of a century ago, when economical methods were not considered essential to industrial life, practically every industry in the whole country was the very synonym of waste and extravagance. Our unparalleled wealth of natural resources, together with high tariff walls, made it unnecessary for manu-

facturers to utilize by-products in order to earn large dividends or to compete with other nations.

It is a remarkable fact that while these great storehouses of natural products had become necessary to the world's industrial progress, in only a few cases were the raw materials converted into marketable products at home. On the contrary, they were sent abroad to be worked up by highly technical institutions, and returned at many times the value of the crude products. In the early years of our industrial development, the very idea of utilizing what was then called industrial waste, seems to have been distasteful to the whole nation. Our manufacturers did not understand the new by-product movement which had given the European nations industrial supremacy; neither were they willing even to try to understand it. They saw only the great treasures stored up in our mines, our forests or in our great fertile plains. They would not see the small but no less important things which belonged to the new by-product movement. It was doubtless this unfortunate condition which kept the highly technical chemical industries from the rapid growth which would have followed under more favorable conditions. With everything at our doors for which a nation could ask, and with a demand for the products which can only be made from by-product waste, it seems strange to the chemist of to-day that our industries should have remained so long in this undeveloped condition. The only logical conclusion which may be drawn is that the American people were either not desirous or not capable of developing the industries to that degree which has made the German Empire what it is to-day.

It should be stated here, in justice to the chemists of the present, and out of genuine respect for the pioneers of the last generation, that the undeveloped condition of our chemical industries can in no way be attributed to them. As a matter of fact, chemists have, throughout the whole of our industrial life, occupied a peculiar position. Their work has been largely a labor of love, a love for the science and a love for mankind; at any rate, they have received little else for their labor. They have repeatedly sounded warning notes of waste and extravagance to the industries and incidentally urged them to employ the new economical methods of manufacture if the United States were to be considered in the industrial race of the future. This frantic appeal to the people of the country to stop the wanton destruction of our national resources has, until recently, been entirely ignored. The classical work of the chemists of the East, with their campaign of industrial education, is having a most wholesome influence upon the eastern industries. The work in the Middle West, North, West and South is likewise having a salutary effect upon the manufacturers, for they are beginning to see that it is better to save at the spigot than it is to save at the bung. On the whole, there is hope of a great industrial revival such as that which has made Germany the greatest of the industrial world-powers.

It is at least encouraging to the chemist at the present time to find that industrial conditions are changing for the better. What changes one can safely predict in the near future may be inferred from the great industrial chemical wave which swept over Germany during the latter half of the 19th century. That magical change which enabled the German people to spring from the fourth to the very first of the industrial world-powers, was due to the wonderful development of their chemical industries and to the amazing methods of conserving their natural resources. Germs of this same reconstruction period, I think, may be found in our own conservation movement. Waste in manufacturing is no longer entirely overlooked by the industries as it was a quarter of a century or even a decade ago.

Notwithstanding the marked improvement in our present industrial condition, it is still evident that industrial conservation will be ignored by the majority of manufacturers unless they have convincing proof that conservative methods mean greater profits and less expense. Their one thought, perhaps a logical one, seems to be of profits. Unfortunately, they have not recognized the fundamental fact that an industry is of vital importance as a national asset only when it conserves the nation's resources and produces the greatest possible returns for the least possible consumption of natural products.

The Wood Industry.—That a revolution of our industrial world has been going on is evident from a study of any one of our great industries. We have already reached the reconstruction period, as is evident from a glance at the greatest of our conservation problems—the wood industry. Fifteen years ago it was impossible to interest lumbermen in any of the wood by-product industries. The real reason seems to have been that the lumbermen found it unnecessary to build up highly technical by-product plants in order to earn large dividends, either in home or foreign markets.

Of the great wastage problems before the American people to-day, wood refuse probably stands first. Few realize the awful waste in the processes used at the present time by the lumbering industries. The industrial chemist is astonished to find that millions of cords of good wood are being burned, either on the ground, where it took hundreds of years to grow, or in huge burners built at the mills for the express purpose of destruction. He is more than astonished to find that laws have been enacted in some of the great timber states compelling the lumbermen to burn all waste wood left on the ground after the logs have been removed. These laws were ostensibly passed for the prevention of forest fires, but doubtless without fully realizing the actual value of the millions of cords of waste.

The term timber has a distinctly local significance. In its broadest meaning, and especially in the great lumbering states of the North, West and South, it represents the forests capable of being converted into lumber. On the Pacific coast, the term is applied only to those mighty forests which have been

growing for a thousand years. On the western plains, any growth of trees, scrub, oak, elm, ash or birch, is called timber. The term is little used in the Middle States, since the depletion of the virgin forests. I have used the word in its broadest sense, as representing trees of all kinds, large or small, which may be converted into marketable products.

Concerning the study of the timber industry of the middle, northern and western states, the writer has had exceptional opportunities. His early years were spent in close touch with lumbering industry of the middle states. Later, on the great plains of the west, he learned the true value of timber. On coming to one of the greatest timber states some seventeen years ago, he realized more fully than ever the frightful waste in the conversion of timber into lumber. With this almost criminal waste of over half of the great forests vividly in mind, he decided to devote some time, at least, to the wood by-product industry. In these early years the task proved so herculean that grave doubts often arose as to whether waste wood from the logging and milling industries could ever be utilized. The work was all the more discouraging on account of the indifference of the lumbermen. They were too busy with the industry as it then existed to give any attention to waste problems. Furthermore, they sincerely believed that wood waste was unavoidable and that its utilization was an absolute impossibility. During these early years, about the only hope of the chemist was in making the lumbermen realize that better and more economical methods were possible and impressing upon them the important fact that wood waste, with proper encouragement, would become the greatest by-product industry in the world.

The important questions which naturally occur to the industrial chemist in these days of conservation are: first, to what extent are the great industries actually wasting our natural resources, and second, can our present industrial methods be so improved as to materially reduce this waste? It requires but a glance to convince one that the waste attending logging and milling industries is the most colossal ever recorded in the history of manufacture. Here, then, is such an opportunity for conservation methods as occurs in no other industry in the country.

It is impossible to even estimate the waste which followed the lumbering industries a single decade ago. A general idea may be obtained of the waste at present, however, by glancing at any of the large mills. The best that these model mills can do to-day, by most rigid economy and by using all the modern improvements known to the industry, is to save a scant 40 per cent. of the total weight of wood in lumber, lath and shingles. Fifteen years ago the average was probably not over 30 per cent.

The Logging Industry.—That the waste wood problem might be more thoroughly investigated, the whole timber industry was studied. Logging, now considered as an entirely separate industry, naturally came first. It was studied in the Middle West and later on the western coast. If the chemist is sur-

prised at the waste produced by the mills, he is simply appalled at the waste which follows the logging industry. It is impossible to give a clear idea of the amount of wood destroyed through the present methods of logging, without details regarding machinery, quality of timber and methods used in different localities, all of which are too technical for this short paper.

The Proportion of Lumber to Waste.—Early in these investigations it was found that no one, not even the lumbermen themselves, knew what proportion of the tree was converted into lumber and what proportion was waste. That at least approximate results might be obtained, several determinations were made, weighing the whole tree so far as possible and the amount of lumber obtained.

The following is an average of three trees:

	Lbs.
Total weight of trees.....	6600
Total weight of lumber.....	2300
Waste.....	4300

Per cent. of lumber, 34.84; per cent. of waste, 65.16.

Stumps, tops, slabs and sawdust are included under waste, but not leaves, twigs, small limbs and small roots. No attempt was made to determine the relative weights of lumber and waste in the large trees of the West, on account of the magnitude of the undertaking, of which one may get an idea from the actual size of the tree. For instance, a Douglas fir stump from the Pacific coast was blasted out and shipped to Minneapolis for experimental purposes. This large stump made nine large dray loads of wood when cut up. To have determined the exact proportion of lumber and waste in this tree would have been a difficult task. Expert lumbermen are inclined to think that the percentage of lumber in these large trees will be somewhat greater than that given above. This will doubtless depend upon conditions. In the case of resinous fir, the trees are frequently cut from ten to fifteen feet above the ground in order to eliminate the resin which exists largely in the roots and the lower part of the trunk. The waste in such cases will exceed the above results.

Waste Wood as Slabs and Sawdust.—While waste wood in the form of stumps and tops represents a large proportion of the total weight of the tree, probably not far from the total weight of the lumber, the actual loss produced in sawing the logs is considerable. From 5 to 15 per cent. of the logs goes into slabs. A part of these slabs is cut into shingles and lath. There is still, however, considerable loss from this source, although less than from the sawdust. The old-fashioned circular saw of thirty years ago cut as high as three-eighths of an inch and the old blade saw even more than that. The waste in sawdust, using a three-eighths inch saw, would probably amount to one-third of the weight of the whole log. The cut has been reduced nearly one-half by the introduction of band, gang and band-gang saws. The waste, however, is still great, not far from 20 per cent. when inch lumber is sawed.

In order to put the waste wood problem in such

form as to give a general idea of the amount of wood destroyed annually by the lumber industries, I have chosen a single locality and a single lumbering plant, calculating results from actual lumbering data. The great mills of the C. A. Smith Timber Company, at Marshfield, Oregon, have been selected because they are recognized by lumber experts throughout the country as the most economical mills in existence. These mills are using every known device which will save a single foot of lumber or a single day's labor. They are among the largest in the world and have been repeatedly called "models of economy." A very brief description of some of the economical machinery will, I am sure, be of some interest to the industrial chemist. The mills are located, as are practically all of the great mills of the country, so that the logs may be transported a part of the way, at least, by water. The trees are felled, cut into as great lengths as possible, and brought down the mountains by means of cables and donkey engines to the logging railroads. They are loaded on specially constructed cars and hauled to the nearest streams of water, where they are thrown in and floated to the mills in booms. At the mill they are cut to proper lengths and split into forms called slips or fliches, by great band saws. These saws are capable of handling logs 80 feet in length and 8 feet in diameter. The slips then go directly to the band-gang or tandem saws. The band-gang saws are entirely new inventions. They are not only more rapid than the old circular and gang saws but also far more economical, wasting approximately 30 per cent. less wood than the old circular saw. From the band-gang saws the lumber is finished by going through the edgers and trimmers.

Of special interest is the lath machinery, consisting of horizontal band saws, which are also an entirely new invention. These saws work automatically and cut 25,000 lath every ten hours. The great importance of this new machinery is its comparative economy. Probably 20 per cent. more lath may be cut from the waste than by the old form.

The Destruction of Waste Wood.—In the early development of the lumbering industries, one of the serious problems which confronted the lumbermen was the disposal of the mill waste, including the sawdust, slabs and bark. In the older mills of fifty years ago, this was hauled away and dumped. A little of it, of course, was used in the mill for fuel, but it has always been regarded by the lumbermen as a nuisance, largely on account of the danger from fire. When the great mills of the Middle West were built, the quantity of sawdust, slabs and bark was so great that the question of its disposal became a serious one. For very good reasons, lumbermen were not permitted to dump any of the waste into rivers or lakes. Some simple means of disposal became absolutely necessary. The so-called waste burner, which was finally devised, has become a regular fixture in the modern lumbering mill. It consists of a vertical cylinder, the size of which depends upon the amount of waste to be burned. The largest is more than

100 feet high, from 40 to 50 feet in diameter, and so constructed that the wood is carried part way to the top and dropped down on the fire below. With a strong draught, the wood burns very rapidly. One may get some idea of the amount of wood burned from the fact that a single large burner will destroy from 800 to 1000 cords in ten hours. Twenty years ago, when the lumbering industry was at its height in Minnesota, there were destroyed at Minneapolis and the neighboring mills 1500 to 2000 cords of waste daily, or enough to have supplied the farmers of the whole state of Minnesota with fuel.

These figures include wastage only from the trees actually felled and transported to the mills for lumber. They do not include the millions of young trees which are destroyed, either by the large falling trees or by the fires which follow in the wake of the loggers. The Bureau of Forestry has called attention to the fact that this destruction of young timber, although minimized by the lumbermen, is, in reality, more vital to the nation than the actual lumber waste, because it seriously menaces the lumber industry of the future generations.

The Annual Wood Wastage.—It seldom occurs, even to the chemist, that wood is by far the most abundant organic substance in the world. The weight of wood or vegetable fiber, as compared with animal matter, is probably not far from a hundred thousand to one. Wood, then, is one of the nation's greatest assets, and its conservation and preservation means the conservation and preservation of the nation's wealth.

The Marshfield mills will again give one a general idea of the waste which accompanies the lumbering industry. This plant saws, on an average, 100,000,000 feet of lumber a year. The average weight of 1000 feet (board measure) of lumber is about one and one-half tons. The annual output of this mill, then, is approximately 150,000 tons of lumber. On the basis of 60 per cent. of waste, the enormous quantity of 225,000 tons of wood are burned, either on the ground where hundreds of years were required for its growth, or in engines of destruction at the mills. A very conservative estimate of the standing timber in this locality, which will eventually be cut by these mills, is 30,000,000,000 feet. Assuming that this timber will all be cut on the above basis, there will be the astounding equivalent of 45,000,000,000 feet of waste which, converted into weight, will amount to the colossal sum of 67,500,000 tons. These figures are enormous, but they seem small when compared with the lumber output during the last decade or even the yearly output. There were cut in 1907, according to the Bureau of Forestry, 40,256,154,000 feet of lumber. On the above basis, there were in that year over 100,000,000,000 feet and over 150,000,000 tons of wastage.

Wood Analyses.—At the time this work was begun there were no analyses of either Norway pine or Douglas fir. The first work on these species was a study of the physical properties of the wood, followed by analyses, including the distillation products, fiber,

the resin and the terpenes. The physical properties of the wood showed a striking variation, even in wood from the same tree. It was not uncommon to find the extreme wood limits of specific gravity in the same tree. A series of determinations on different parts of the same tree gave the following:

	Fir.	Norway.
Specific gravity of very lean wood	0.6074	0.6025
Specific gravity of medium wood	0.6711	0.6432
Specific gravity of resinous wood	0.8225	0.7984
Specific gravity of very resinous wood	0.9456	0.9322
Specific gravity of green roots, very resinous	0.9746	0.9721

The above averages of five different determinations indicate that the two species are quite similar. There was a difference, however, in distribution of the resinous matter. The Norway pine was quite uniform, the stumps and the roots being nearly always resinous. The fir, on the contrary, was extremely variable. It was not uncommon to find parts of fir trees containing as high as 50 per cent. of oleoresin, while other parts of the same tree contained as low as 3 per cent.

The first resin and terpene analyses were made for the purpose of determining the relative amounts of resin and terpenes in the various samples of wood, and further for the purpose of studying the physical and chemical properties of the resin and the terpenes themselves. These determinations were made by extracting the wood in large modified forms of Soxhlet extractors, using the various organic solvents. An average of some twenty analyses gave the following:

	Lean wood.	Resinous wood.	Average wood.
Per cent. of oleoresin in Norway pine	6	43	14
Per cent. of oleoresin in Douglas fir.	4	46	16

The amount of oleoresin in the average wood will be seen to be considerably less than the mean of the lean and the rich wood. This was found to be due to the fact that the greater portion of the wood was lean. These results were all obtained from stumps. Analyses of the trunks themselves gave considerably lower results. Parts of the tree near wind-shakes, however, gave even higher results than the stumps. A single analysis of a resinous wind-shaken tree from the Puget Sound district gave 52.5 per cent. of oleoresin. The oleoresin was finally subjected to steam distillation and the amounts of resin and terpenes determined:

	Fir.	Norway.
Per cent. of resin in oleoresin from	78	78
Per cent. of terpenes	22	22

These results are an average of many determinations and indicate that the proportions of resin and terpenes are practically constant in oleoresin fresh from the tree. The terpenes decrease slowly on exposure to the air. An analysis of wood from a stump twenty years after the tree had been cut showed 42.4 per cent. of resinous matter, 21 per cent. of which was turpentine. The only part of this stump which seemed to have changed was the surface; here the resinous matter had become hard and impervious to both air and water.

The Turpene.—The terms turpene and turpentine have been used synonymously for the reason that the turpentine from the northern species is complex, containing several high boiling terpenes. Common turpentine has been so closely associated with so many branches of industrial art that, were it taken away, the loss would be irreparable unless some good substitute could be found. At the present time nearly all the turpentine is obtained from the forests of the South. The old method of boxing sooner or later kills the tree. In the early history of the industry, three or four years was the average life of the boxed tree. Much better results are now obtained by the new methods of turpentine orcharding. A few years ago, the destruction of the forests of the South was so rapid that the United States government became alarmed lest the turpentine industry should be completely destroyed.

At the present time, the northern and western states play a very small part in the resin and turpentine production of the country, but, as has already been stated, these northern species contain large quantities of both resin and turpentine. Owing to the peculiarities of the species, however, their recovery becomes strictly a problem of by-product chemistry. In fact, resin and turpentine are abundant enough in both the Norway pine and the Douglas fir to make them an important factor in the resin and turpentine output of the country, if economical methods for their recovery were used.

Using again the lumbering plant above mentioned, some idea may be obtained of the amount of resin and turpentine wasted by the lumbering industries of the West. Probably one-fifth of the fir and Norway pine waste wood is rich enough in oleoresin to make its recovery profitable, even by the old process of destructive distillation. While the average of oleoresin in the northern species of pine can only be approximated, over one hundred analyses of wood of all kinds and degrees of resinousness indicates that one-fifth of the fir wood waste from the Puget Sound district contains twenty per cent. of oleoresin. On the above basis, there are 45,000 tons of rich resinous wood, containing 9,000 tons of oleoresin, of which 1,980 tons are turpentine, destroyed annually by the above-mentioned mills. This does not include the resinous matter in the other four-fifths of the wastage. If the standing timber in the locality be again taken at 30,000,000,000 feet, the wastage would at the present rate of lumbering amount to 67,500,000 tons. One-fifth of this waste, or 13,500,000 tons, is sufficiently rich in resinous matter to warrant the use of any good method for its recovery. Assuming that this amount will average even 10 per cent. of oleoresin, there would be the enormous sum of 1,350,000 tons of resinous matter, of which 22 per cent., or 297,000 tons, are turpentine. Translated into common terms, it reaches the colossal sum of over 80,000,000 gallons. Again, assuming that the annual consumption of turpentine is 21,000,000 gallons, the above amount would supply the whole world for nearly four years.

Present Methods of Utilizing Waste Wood.—There are numerous methods of utilizing waste wood at the present time, but the more important may be grouped under the following heads:

1. Fuel, yielding heat and power.
2. Destructive Distillation, yielding charcoal, and distillates, as tar, wood alcohol and pyroligneous acid.
3. Extraction, yielding resinous matter, turpentine, wood pulp.

Fuel.—The present generation is truly one of conservation, for men are beginning to estimate everything from the energetic point of view. Coal, for instance, is bought to-day largely on the basis of the amount of heat energy it will produce. Waste wood becomes significant even when considered from the standpoint of heat energy for the amount of energy wrapped in our forests is incalculable. An idea of the loss of energy in waste wood may be obtained by determining the amount of heat energy liberated when wood burns. The heat of combustion of average fir wood is about 7,800 British thermal units per pound of wood. This heat energy may be converted into ergs or into horse power, a more familiar term; or better, it may be converted into the equivalent of bituminous coal. Good coal yields about 13,000 British thermal units per pound of coal. One ton of wood will then be equivalent to six-tenths of a ton of coal. If the total annual waste, above mentioned, be translated into the equivalent of bituminous coal, it will amount to the enormous sum of 90,000,000 tons.

Destructive Distillation.—Destructive distillation of wood has been used for centuries. Primarily, the object was to obtain charcoal, although in some cases distillation of hard wood was carried on for the purpose of obtaining the distillates. Destructive distillation in retorts on a large scale is a distinctly modern process and is one of the most important by-product industries. The distillation of coal by the closed retort process yields by-products of greater value than the coke itself.

At the time these experiments were begun, the only means of utilizing waste wood of any kind in this country, so far as I am aware, was by destructive distillation. It was soon found that the distillation of pine wood was quite a different process from the distillation of hard wood. In the distillation of hard wood, it makes comparatively little difference how the heat is applied to the retort so long as the temperature is raised sufficiently high to drive off all the distillates. The distillation of pine wood, on the contrary, is different. The nature and the yield of tar, and more especially terpenes, were found to be largely dependent upon the manner of heating the wood.

In order that definite results might be obtained concerning the manner of heating the wood, experiments were made in a small retort, so arranged that the retort could be heated to a red heat in a few minutes. The amount of turpentine, tar and acids was greatly reduced by this rapid heating. A sam-

ple of wood containing 50 per cent. of oleoresin, 11 per cent. of which was turpentine, was suddenly heated to a bright red heat, yielded less than half of the total weight of resin in tar and only a quarter of the total amount of turpentine. The yield in the same sample of wood was nearly doubled by slow and cautious heating.

Having found that the yield of by-products is largely dependent upon the manner of heating, experiments were next made with different shaped retorts, in order that the best and most efficient form might be determined. The one which gave best results was so constructed that the temperature of the wood could be gradually raised to the distilling point. This was accomplished by using a long inclined cordate tube retort, the lower end of which could be heated to a red heat, while the upper end could be kept moderately cool. The retort was arranged so that the wood was admitted at the upper or cool end, gradually passing downward by gravity and by a mechanical device until it reached the lower or red hot end of the retort. By this means, the least possible amounts of both resin and turpentine were decomposed. The retort was also constructed so that the oleoresin could escape from the retort without being distilled. To accomplish this, openings were made in the cordate lobes of the upper end of the retort, in order that the oleoresin when removed from the wood, by "trying out," might pass through these bottom openings instead of passing through the ones in the top of the retort by vaporization. It was found that a portion of oleoresin could be removed by this process with but slight indications of decomposition. The amount of tar was increased, its quality improved and nearly all of the turpentine was recovered.

In order to obtain as accurate data as possible, waste pine wood from the forests and mills of the North and West was subjected to destructive distillation and the distillates as well as the charcoal determined. The following table is a comparison of the results obtained by distilling the three common species:

	Norway pine. Lbs.	Southern pine. Lbs.	Douglas fir. Lbs.
Weight of wood taken.....	100	100	100
Charcoal.....	24	22	24
Gaseous products.....	25	26	24
Tar and terpenes.....	19	14	14
Pyroligneous acid, including water	37	38	38

From these results it will appear that the three species of pine are very nearly alike. Each sample was what would be called resinous wood. The samples of the northern and western wood were largely taken from the stumps although some were from the resinous part of the tree. The southern samples were confined to the trunks of several trees brought from the turpentine forests of Florida. The yield of turpentine in each case was somewhat less than the total amount existing in the wood or obtained by either steam distillation or by extraction. The loss was found to be due to the decomposition of the oleoresin by heat. This was especially noticeable when the distillation took place rapidly. For instance,

wood containing 1 per cent. of turpentine only yielded 2 per cent. by rapid distillation.

While the retort described gave very satisfactory results so far as by-products were concerned, the chief difficulty lay in the market value of the products. The tar, which has a real value abroad and even in the South, was found to be practically worthless in the North and West, despite the determined efforts to utilize it in the paint, wood preservation and other industries. Most of the distillation plants of the North and West actually burn the tar and throw away the pyroligneous acid. As pine wood yields only a trace of alcohol, the only marketable products left are the turpentine and charcoal. The latter, however, has little value, hence the whole process of pine wood distillation in the North resolves itself into the recovery of the turpentine. As a considerable quantity of the turpentine is lost, even by the most improved processes of distillation, other methods of utilizing the waste wood seemed absolutely necessary. The above experiments are of some interest, however, because they were the first made on the wood of the northern and western species of pine and incidentally show that the yield of gaseous as well as other products is dependent largely upon the method of distillation.

Realizing, after years of labor in perfecting apparatus for the economical distillation of pine wood, that some other process than distillation must be found if the waste wood of the North and the West is to be converted into products of any economical value, the whole plan was changed from distillation to extraction. The reason for the change is evident from a comparison of the products obtained by the two processes. As has already been stated, the only real marketable product obtained by distillation is turpentine. By the extraction process, practically all of the wood is converted into commercial products, namely, resin, turpentine and wood fiber, any one of which is worth more at least in the North than all of the distillation products.

At the time this work was begun there was little hope of an extraction process which could be used for the recovery of both the resin and the terpenes. The cost, with the losses which necessarily follow a process of this kind, excluded the use of all of the common solvents. The first experiments made along this line were with steam. It was found that the terpenes could be easily removed from the wood by superheated steam. That definite results might be obtained, retorts were built so that steam could be passed through them under pressure. The wood was chipped into small pieces, placed in these retorts and distilled with superheated steam. The terpenes were quickly and quantitatively removed. The difficulty with this process was that the resin still remained in the wood and some method for its recovery was necessary before the process could be considered satisfactory. The only solution, therefore, was in the use of the common solvents.

As the steam process required two separate operations, experiments were made, excluding the steam

and using the solvents direct. All of the common solvents were tried, among them, petroleum ether, benzene, ether and carbon disulphide. It is worthy of note that in the early stages of this work the cost of benzene entirely excluded its use. Later, however, the supply of crude benzene from the coke industry made it more satisfactory than its sister solvent, petroleum ether.

After trying various forms of apparatus, one depending upon common extraction principles was adopted as giving best results. The apparatus was so constructed that several extraction chambers, arranged somewhat after a beet sugar diffusion battery, were connected with a large steam-heated boiler containing the solvent. The arrangement was such that by heating the boiler, the vapors of the solvent could be forced through any one of the extraction chambers containing the wood, where the vapors were condensed and returned to the boiler laden with the oleoresin. After the extraction was completed, the last traces of the solvent were removed by forcing through the wood, air, steam, and finally, hot alkali, for the conversion of the wood into pulp. By this treatment all of the resinous matter was removed, the solvent recovered with very slight loss, and the wood was converted into pulp.

The terpenes of both the Norway pine and the Douglas fir have already been described.¹ The properties of the terpenes obtained by extraction were identical in every respect with those obtained by boxing. The resin from the Norway pine has likewise been described.² The resin from the Douglas fir, under examination at present, resembles the resin of the southern pine. It is composed chiefly of abietic acid with an acid of unknown composition and a small quantity of unsaponifiable matter.

Paper from Waste Wood.—The paper industry has become one of the greatest and most important parts of our commercial fabric. But a few years ago, nearly all of the paper was made from cotton and linen rags, hemp, flax and jute. Very little paper was made from wood pulp. At the time this work was begun there was not a single pulp mill in the whole northwest. They are now counted by the score. Spruce wood is chiefly used in this locality for the reason that it is readily reduced and requires little bleaching. Spruce, however, is becoming scarce. The price has nearly doubled within the last five years. At the present rate of consumption, all of the spruce wood in Minnesota, Michigan and Wisconsin will have been used up within the next decade and other sources must be found. White pine, cottonwood, basswood, hemlock, birch and even soft maple give perfectly satisfactory results. As a matter of fact, any wood belonging to the pine family may be used. Even the stumps, roots and branches of the Norway pine and Douglas fir make an excellent grade of pulp when properly treated.

In studying wood waste with the idea of converting the fiber into pulp, various methods for the manu-

facture of paper were tried. The sulphite process, the one universally used in the northwest, was thoroughly tested. It proved unsatisfactory on account of the fact that even a very small amount of insoluble resinous matter turns black in sulphite solution. The soda process, with certain modifications, was found to work satisfactorily and especially with extracted wood. A number of pulp determinations were made, using wood from different parts of the tree. An average of several determinations gave the following:

Wood pulp in	Per cent.
Norway pine stumps.....	27
Douglas fir stumps.....	24
Fir sawdust.....	22
Southern pine.....	23

The highest yield of 43 per cent. of fiber was obtained from lean fir wood, thoroughly seasoned, while the lowest, of 16 per cent., was obtained from green resinous fir. It was found by actual test that the fiber from this waste wood was equal to the best obtained from spruce, by either the sulphite or the soda process. Recent experiments show that even sawdust, by careful treatment, yields a fiber of good enough quality to make any of the common paper.

If waste wood is again considered from the standpoint of paper, its economic value is greatly magnified. Some idea of the total waste from the paper point of view may be obtained by again using the annual waste from the above-mentioned mills. Of the 225,000 tons of waste wood, at least one-half can be converted into pulp at a minimum cost. From actual experiments, this waste averages 22 per cent. of pulp. The annual amount of pulp wasted in this one locality, then, is little less than 25,000 tons. When one finally considers the total waste throughout the North, West, and South, the waste wood problem from the paper side alone looms up as one of the most vital problems with which the American people have to deal.

In conclusion, I will state that the technical and minor details have been purposely omitted. The chief object of this general résumé of work which I have been carrying on for a number of years is to interest my colleagues in the great wood problem. If waste wood is to be converted into its most valuable by-products, industrial chemists must join in the work. There are hundreds of uses to which this waste may be put when once this great problem is exhaustively studied.

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COMMERCIAL BENZOL IN THE UNITED STATES.¹

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Benzol is a general commercial name applied to the liquid aromatic hydrocarbon mixtures derived from coal tar light oil. It is the purpose of this paper to consider briefly the manufacture, classifica-

¹ *J. Am. Chem. Soc.*, **28**, 1467.

² *Ibid.*, **31**, 561.

¹ Presented October 10, 1910, at the meeting of the Philadelphia Section of the American Chemical Society.

tion, properties and commercial uses of the various grades of benzol.

Coal tar light oil is a liquid varying in color from straw to nearly black. Its gravity is less than that of water, and it has a pungent, somewhat unpleasant odor. It is of indefinite constitution, according to the nature of the tar from which it is distilled, but varies rather as to proportion than as to nature of its constituents. It is mainly composed of (1) phenolic acid bodies known as tar acids, of which phenol and the three isomeric cresols are the main constituents; (2) aromatic bases, of which pyridine is the best known type; (3) unsaturated bodies of the type of styrol; (4) aromatic hydrocarbons, as benzene, toluene, xylene, cumene, etc.

This last class of compounds forms the basis of the commercial benzols. Only the first three are separated in the pure state. Benzene and toluene, known in commerce as pure or C. P. benzol, and toluol, are produced in an almost pure state, with less than 0.5 per cent. of impurities. These boil entirely within 2°. Pure xylol consists of a mixture of the three isomeric xylenes, and has a boiling point range of 135°–145° C. No attempt is made in this country to separate the three isomers. The other grades of benzol are classified according to the boiling point.

One hundred per cent. benzol, 90 per cent. benzol and 50 per cent. benzol are mixtures of benzene, toluene and xylene, and their names indicate the amount distilling under 100° C. In addition to these we have commercial toluol and solvent naphtha or 160° benzol. The former is composed mainly of toluene and has a distillation starting at 100° C. and giving 90 per cent. at 120° C.; the latter on distillation test shows a few per cent. at 130° C. and 90 per cent. at 160° C., and mainly contains xylenes and cumenes.

All the above products are highly refined, are water white, and have a pleasant aromatic odor. In addition to these there are straw-color products, known as straw-color benzol and straw-color toluol. These have a poorer odor and contain some unsaturated compounds. The straw-color benzol corresponds in boiling point to 90 per cent. benzol, and the straw-color toluol to commercial toluol.

Two darker naphthas are also produced, one a crude product about corresponding in boiling point to solvent naphtha. It is a dark oil, of about the same evaporative power as turpentine. The other dark naphtha, known generally as heavy naphtha, is heavier than any I have previously mentioned. In boiling it tests a few per cent. at 160° C., and about 85 per cent. at 200° C.

The first process to which light oil is subjected is a preliminary distillation to remove tarry matter, and any heavy oils and naphthalenes. The distilled oil is then treated in lead-lined agitators with dilute sulphuric acid, to remove pyridine and other bases. This is followed by a treatment with caustic soda solution, by means of which the tar acids are removed, and this solution of carboic acids in soda forms the

crude material, from which is made crystal carboic acid and cresols.

The extracted neutral oil is then subjected to a series of fractional distillations, by means of which it is split up into various fractions of different boiling points. This is carried on in column stills resembling those used in alcohol rectification, and it is at this point that the various straw-color and dark products are taken off.

These crude fractions are then chemically washed with strong sulphuric acid, which has the effect of removing unsaturated compounds and leaving the aromatic hydrocarbons, which only require a distillation to remove any tarry matter formed by the action of the acid to give the water-white, refined products. For the pure or C. P. grades, a further column distillation is required, using for this purpose a refined fraction rich in the material sought after.

Before tabulating the most important properties of these various grades of benzol, it might not be amiss to give here the methods of testing used:

(a) Boiling point: 100 cc. of benzol are taken in a 200 cc. glass distilling bulb protected from superheating by an asbestos ring, and connected to a 24" water-cooled condenser. A thermometer is placed with the top of the bulb opposite the exit tube of the flask. The distillation is started and run as fast as separate drops will form. The distillate is collected in a 100 cc. cylinder and the temperature at which the first drop falls is noted and thereafter the per cent. distilled at every even 10° until dry. The temperature at the drying point is also recorded. For C. P. grades finer thermometers are used and readings taken every 1/5° C.

(b) Specific gravity: Taken with a hydrometer or Westphal balance at 15° C.

(c) Flash point: Taken in a Tagliabue open cup tester in the usual way.

(d) Sulphuric acid test (taken on refined grades only): 7 cc. of C. P. 66° H₂SO₄ are shaken with 21 cc. of benzol in a small stoppered bottle, and the coloration, after standing 15 minutes, noted. With pure benzol, toluol and xylol, the coloration of the acid is at most a very pale straw; with the commercial grades of refined benzol, except solvent or 160° benzol, the acid may be somewhat darker, but the oil should remain white; with solvent naphtha the oil turns a little yellow and the acid colors red.

(e) Evaporation test: This is taken by noting the time required for 2 cc. of the benzol to evaporate from a metal surface with raised edges 3.5" square. It should, to allow for variation in temperature, be compared to pure benzol, which requires 10 minutes for complete evaporation at ordinary laboratory temperatures.

(f) Freezing point: This is taken only on pure benzol. About 50 cc. are taken in a large test tube and cooled down, stirring with a thermometer in the liquid. Pure benzol should solidify and show a constant temperature at about 5° C.

In Table I, I show the range of boiling points, gravities and flash points of the various grades of ben-

zols, and in Table II, the evaporation on all these benzols, along with similar tests on turpentine and several grades of petroleum naphtha.

Unlike the petroleum series, the gravities on the refined grades decrease with increase of boiling point,

stain solvents used to dissolve the dry color. Enamel paints also very often have benzol as a part of their make up, as well as bronze and aluminum paints. The basis of these paints is a concentrated solution of gum, usually damar, and as benzol has a strong

TABLE I.—BOILING POINTS, SPECIFIC GRAVITIES AND FLASH POINTS OF BENZOLS.

	Boiling point.	Gravity at 15° C.	Flash point.
Benzol, pure.....	80° to 82° C.	0.881 to 0.884	Below freezing
Benzol, 100 per cent.....	109 per cent. at 100° C.	0.875 to 0.884	Below freezing
Benzol, 90 per cent.....	90 per cent. at 100° C.	0.875 to 0.882	Below freezing
Benzol, 50 per cent.....	50 per cent. at 100° C.	0.871 to 0.875	Below freezing
Toluol, pure.....	110° to 112° C.	0.869 to 0.871	Below freezing
Toluol, commercial.....	90 per cent. at 120° C.	0.869 to 0.872	Below freezing
Xylol, pure.....	135° to 145° C.	0.865 to 0.867	85.5° F.
Solvent naphtha or benzol 160°.....	90 per cent. at 160° C.	0.864 to 0.870	78° F.
Benzol, straw-color.....	Like 90 per cent. benzol	0.862 to 0.870	Below freezing
Toluol, straw-color.....	Like commercial toluol	0.862 to 0.870	Below freezing
Crude solvent naphtha.....	Like solvent naphtha	0.876 to 0.887	78° F.
Heavy naphtha.....	About 85 per cent. at 200° C.	0.925 to 0.940	109° F.

while the evaporation table runs over a wide range so that a benzol for any particular purpose can be readily selected.

The principal use of the various grades of benzol is as a solvent. Benzol is an excellent solvent for gums and resins, oil-aniline colors and rubbers.

TABLE II.—EVAPORATION TESTS.

	Minutes.
Pure benzol.....	10
100 per cent. benzol.....	13 1/2
90 per cent. benzol.....	14
50 per cent. benzol.....	23
Pure toluol.....	29
Commercial toluol.....	33
Xylol.....	89
160° benzol or solvent naphtha.....	107
Straw-color benzol.....	18
Straw-color toluol.....	36
Crude solvent naphtha.....	121
Heavy naphtha.....	303
Turpentine.....	142
80° gasoline.....	4
70° gasoline.....	8
66° benzene.....	16
62° benzene.....	18

Pure benzol and toluol are used as the basis of manufacturing other chemicals, such as nitrobenzol, aniline and benzoic acid, etc. They are also used for solvents where a very high grade of purity is demanded, such as crystallizing drugs and chemicals. Then also where a continuous solvent recovering extraction process is used, a uniform low-boiling material is necessary, and for these purposes pure benzol has been found of great value. Pure benzol is also used as a solvent in the manufacture of cements and coatings for food product cans—being the only practical material pure enough for this purpose.

The other commercial refined benzols are used in various industries, as solvents or thinners, the grade selected being conditioned by the particular needs of the material being manufactured.

In the paint and varnish industry the uses of benzol are varied. In certain varnishes benzol is often used as a thinner, to cheapen the turpentine, being preferred to petroleum benzine because this latter substance has not the power of holding certain gums in solution that benzol has. Benzol is also largely used in wood stains, owing to the great solvent power it has for the oil-soluble aniline colors. For the same reason it is largely the basis of many commercial

solvent action on this material, it is a very desirable material to use. Then the strong solvent action of benzol makes it an excellent base for varnish removers, and there are many patents covering its use in this connection. For all these purposes the grade of benzol to be selected depends largely on the drying effect desired. All have approximately equal solvent power, so that the rate of evaporation is the important conditioning factor. Mostly water-white or refined grades are used, owing to their greater purity; but in some cases where color and odor are not essential, straw-color grades are used. For tar paints, gilsonite paints, etc., straw-color benzols, and the darker, heavier naphthas are almost exclusively used. The dark naphtha, corresponding to solvent, is largely used as a turpentine substitute, where odor and color are not important features, especially as a thinner where the varnish or paint is not to be sold but to be used in the maker's own factory. Heavy naphtha is mainly used in ship-bottom paints, and in thinning coal tar paints and varnishes.

Then in another field benzol has very large application. Though it does not dissolve pyroxylin or soluble cotton, yet the amyl acetate solutions of this material can be thinned to a greater extent by benzol than by any other commercial solvent. To this property is due its large use in two industries—lacquers and imitation leather. A number of lacquers are only soluble cotton dissolved in amyl acetate and thinned with benzol. Many imitation leathers have as their base such a solution which is applied to cloth, and the resulting coating colored and grained in various ways. Even in the imitation leathers which have a linseed oil base, benzol is largely used as a solvent. In the first class of imitation leathers only refined benzols are used, while in the latter class straw-color benzols also find application.

Benzol is also a perfect rubber solvent. The only commercial article which equals it in solvent power is carbon bisulphide, and this has the disadvantages of being much more expensive and very much more dangerous to handle; so in all high-class rubber cements we find benzol used. The advances in the automobile tire industry have opened up a new and large market for benzol, for in this field benzol is indispensable. Along these lines, too, are rubber solu-

tions, used as the base of insulating varnishes. Here also benzol finds application. Somewhat allied are solutions for cold vulcanization of rubber, which are essentially mixtures of benzol and sulphur monochloride. For all these purposes the refined grades are mostly used.

Other uses of benzol which I may briefly mention are in the composition of metal polishes and metal protective coatings, dry cleaning and scouring, grease extraction, and in coatings for wooden forms used in concrete construction. This last use is a recent one, and where tried has apparently given satisfaction, and this field may be capable of enormous development.

Benzol viewed from a commercial standpoint is really only in its infancy in this country. As time progresses and new sources of supply are opened up, new and larger uses will have to be found for it. On its large and varied solvent power rest its capabilities for further commercial utilization, and to this feature is due the rapid growth of the industry in this country.

BARRETT MFG. CO. LABORATORY,
CHEMICAL DEPARTMENT,
FRANKFORD, PA.

TIME, TEMPERATURE AND COMPOSITION AS FACTORS IN SOFTENING WATER.¹

By J. C. WM. GRETH.²

Received November 1, 1910.

The problem of softening and purifying water is much more difficult than at first appears to the novice.

The complexity of the impurities and the wide variations in waters from the same sources of supply do not admit of the application of a fixed method for all waters.

The softening of water is understood by many to be merely a question of the addition of lime and soda ash. This is shown by articles in engineering and chemical journals and even government publications, advising the use of so much lime and soda ash for a certain water supply. Looking at the problem from this point of view, the question naturally arises among engineers and water users as to the necessity of the apparatus for the proper softening and clarification of water.

In softening water we have to deal with extremely dilute solutions which are made complex by the number of substances in solution, each to some extent affecting the solubility of the other.

To remove the various salts of lime and magnesia from the dilute complex solutions by means of the two reagents, commercial caustic lime and soda ash, both of which, especially the former, are likely to vary in purity, calls for an accurate method of control, and a wide experience with different waters.

Chemists usually estimate the quantity of reagents required on the basis of the molecular weights of the lime, magnesia and iron salts in the water. It has been my experience that no fixed rules, applicable to all water supplies, can be laid down as to the exact

quantity of reagents required, the method of controlling treatment, the time required for reactions and sedimentation, or for perfect clarification.

The time to be allowed for the complete softening of the water must be determined. No definite time can be set as being sufficient for all waters unless, of course, sufficient time is allowed in all cases to take care of those waters which require the maximum time for complete reaction.

This would hardly be practicable, as the cost of the water-softening system must be considered, and this cost is, in a large measure, dependent on the time allowed for reactions. In many types of water-softening apparatus on the market, the time allowed for reactions has been the uncertain minimum rather than the safe maximum.

That the time allowed for reactions is a question of vital importance, and that it has received little attention, is evidenced by the fact that in many cases a softened water will leave the water-softening apparatus, as it should, perfectly clear; but after standing for a time it becomes turbid, and eventually a deposit is found in the container. This can be seen in many of the track tanks of railroad companies, or in the storage tanks of industrial plants, using water-softening apparatus. In some cases this becomes a serious annoyance and expense.

Again, deposits from softened water are found in feed-water heaters, and in pipe lines connecting the heater and boilers. Reference is not made here to a precipitate due to the reduced solubility of the lime and magnesia salts at the higher temperature, but to precipitation due to the continued reaction between the softening reagents and the lime and magnesia in the water. Moreover, sludge is deposited in the boiler. While this cannot be entirely prevented, yet in some cases the amount of sludge thrown down almost makes one believe that a boiler compound and unsoftened water had been used in place of a softened water. Again, it is extremely common in many water-softening systems to find even the pipe carrying the softened water from the system to be choked with scale. These effects are undoubtedly due to insufficient time for reactions within the softening apparatus.

Temperature is, of course, a factor in the time to be allowed, but in almost all cases it is desirable to soften the water before it is heated; therefore, the softening reactions must take place at temperatures between 32° and 85° F.

Every expedient known to the chemist and engineer must be employed in the design of apparatus to properly soften water on a large scale in a reasonable time. All chemists will agree that the addition of the reagents must be exact and that they must be thoroughly mixed with the water. It would seem but rational to suppose that in the laboratory with a small sample, following the method employed on the large scale, ideal results could be obtained and that these results might be used as a basis for designing water-softening apparatus, at least, as far as the time to be allowed for reactions is concerned, but let us

¹ Read before Pittsburgh Section of the American Chemical Society.

² Manager Water Purifying Dept., Wm. B. Scaife & Sons Co.

see what actually occurs in attempting to treat a small sample of water in the laboratory, following as closely as possible the practice which gives results on the large scale.

The following analysis of a well water with data showing the extent of the reactions for given periods of time has been selected from a large number of waters on which similar experiments have been tried to determine what can be done in the laboratory in attempting to parallel the results obtained on a large scale:

DETERMINATIONS.

	Parts per million.	Grains per U. S. gallon.
Volatile and organic matter.....	75	4.40
Silica.....	9	0.55
Iron and alumina oxides.....	trace	trace
Calcium oxide.....	158	9.30
Magnesium oxide.....	165	9.72
Sodium oxide.....	20	1.15
Sulphuric anhydride.....	343	20.20
Carbonic anhydride (fixed).....	123	7.26
Carbonic anhydride (free).....	none	none
Chlorine.....	12	0.70
Alkalinity as CaCO ₃	281	16.50
Total solids by evap.....	896	52.70

PROBABLE COMBINATIONS.

	Parts per million.	Grains per U. S. gallon.
Volatile and organic matter.....	75	4.40
Silica.....	9	0.55
Iron and alumina oxides.....	trace	trace
Calcium carbonate.....	281	16.53
Calcium sulphate.....	2	0.10
Magnesium sulphate.....	496	29.16
Sodium sulphate.....	21	1.24
Sodium chloride.....	20	1.15
Total solids.....	904	53.13
Suspended matter.....	1	0.05
Free carbonic acid.....	none	none
Incrusting solids.....	788	46.34
Non-incrusting solids.....	41	2.39

The experiments on this water were made at temperatures ranging from 50° to 60° F. Under the heading "Boil," the sample had stood for 24 hours, then 100 cc. of it were brought to a boil, cooled, then filtered, and the determinations made.

	1 hour.	2 hours.	3 hours.	4 hours.	24 hours.	Boil.
CaO.....	51a 3.00b	26a 1.50b	26a 1.50b	17a 0.98b	14a 0.84b	10a 0.56b
MgO....	53a 3.10b	10a 0.60b	10a 0.60b	5a 0.30b	5a 0.30b	3a 0.20b

These experiments were made on rather bad water, in fact water worse than the average. Now let us see the results of the same experiments on a water considerably better than the average, under a similar set of conditions, a river water.

DETERMINATIONS.

	Parts per million.	Grains per U. S. gallon.
Volatile and organic matter.....	9	0.55
Silica.....	8	0.45
Iron and alumina oxides.....	2	0.10
Calcium oxide.....	14	0.84
Magnesium oxide.....	3	0.18
Sodium oxide.....	1	0.07
Sulphuric anhydride.....	7	0.44
Carbonic anhydride (fixed).....	7	0.44
Carbonic anhydride (free).....	2	0.11
Chlorine.....	5	0.30
Nitric anhydride.....	2	0.10
Alkalinity as CaCO ₃	17	1.00
Total solids by evap.....	53	3.10

a Parts per million.

b Grains per U. S. gallon.

PROBABLE COMBINATIONS.

	Parts per million.	Grains per U. S. gallon.
Volatile and organic matter.....	9	0.55
Silica.....	8	0.45
Iron and alumina oxides.....	2	0.10
Calcium carbonate.....	17	1.00
Calcium sulphate.....	11	0.68
Magnesium sulphate.....	1	0.06
Magnesium chloride.....	5	0.29
Magnesium nitrate.....	2	0.14
Sodium chloride.....	2	0.13
Total solids.....	57	3.40
Suspended matter.....	9	0.55
Free carbonic acid.....	2	0.11
Incrusting solids.....	47	2.72
Non-incrusting solids.....	2	0.13

	1 hour.	2 hours.	3 hours.	4 hours.	22 hours.	Boil.
CaO.....	39a 2.30b	39a 2.30b	39a 2.30b	39a 2.30b	36a 2.10b	33a 1.96b
MgO.....	3a 0.20b	3a 0.20b	3a 0.20b	3a 0.20b	3a 0.20b	3a 0.15b

From these experiments it would seem that at the end of two hours the treatment is practically completed. But the fact that a further reduction in both the calcium and magnesium oxides takes place after the end of two hours shows that the reactions are not entirely completed, and it is probable that just at this stage many water-softening machines stop in place of allowing sufficient time for the reactions to be completed.

The amount of impurity in the water is also a factor in the time to be allowed in softening a water. This is illustrated by the second analysis just cited. In this experiment, after allowing 22 hours for the reactions to complete themselves, and heating the water to a boil, the total of the calcium and magnesium oxides is higher in the treated water than in the raw water, while in the first experiment the total of the calcium and magnesium oxides is lower in the treated water than in the raw water of the second experiment, showing that other factors besides time and temperature enter into the completeness of the softening.

As these experiments were conducted in exactly the same manner, and the conditions kept as nearly uniform as possible, one would have expected the results to be the same.

The results of such experiments, therefore, serve only as a guide which enables one having before him a large number of similar results, based on like experiments to draw conclusions, first, as to the length of time required on a large scale for complete reactions, and second, as to the minimum to which the calcium and magnesium oxides can be reduced in the treated water.

After the time to be allowed for reactions has been determined, provision must be made for sedimentation and efficient clarification to carry the process to its logical conclusion, which is to remove the lime and magnesia as well as all suspended matter, to the extent that no after-precipitation can occur.

The following analysis shows a water very similar to the one cited for the second experiment:

a Parts per million.

b Grains per U. S. gallon.

DETERMINATIONS.

	Parts per million.	Grains per U. S. gallon.
Volatile and organic matter.....	27	1.60
Silica.....	9	0.55
Iron and alumina oxides.....	2	0.10
Calcium oxide.....	12	0.70
Magnesium oxide.....	5	0.32
Sodium oxide.....	21	1.24
Sulphuric anhydride.....	35	2.04
Carbonic anhydride (fixed).....	4	0.22
Carbonic anhydride (free).....	6	0.33
Chlorine.....	12	0.70
Nitric anhydride.....	trace	trace
Alkalinity as CaCO ₃	9	0.50
Total solids by evap.....	121	7.10

PROBABLE COMBINATIONS.

	Parts per million.	Grains per U. S. gallon.
Volatile and organic matter.....	27	1.60
Silica.....	9	0.55
Iron and alumina oxides.....	2	0.10
Calcium carbonate.....	9	0.52
Calcium sulphate.....	17	1.00
Magnesium sulphate.....	16	0.96
Sodium sulphate.....	25	1.44
Sodium chloride.....	20	1.15
Total solids.....	125	7.32
Suspended matter.....	9	0.55
Free carbonic acid.....	6	0.33
Incrusting solids.....	54	3.13
Non-incrusting solids.....	44	2.59

This water, after treatment with lime and soda ash in a four-thousand gallon per hour water-softening system, in which a time of four hours is allowed for the softening, shows calcium oxide 9.5 parts per million; magnesium oxide, 1.4 parts per million; corresponding to calcium carbonate, 17 parts per million; magnesium hydrate, 2 parts per million; so here are two waters very much alike as to total hardness. One water under laboratory conditions is harder after treatment, allowing a longer time for reactions even with the aid of heat, while on a large scale a similar water is softened at atmospheric temperature, and in a much shorter time, to such an extent that both the calcium carbonate and the magnesium hydrate in the water are lower than the solubility of each of these substances in distilled water.

This is almost invariably the case, and proves that in a properly designed water-softening system a softer water can be obtained than by laboratory experiment conducted along correct, scientific lines, paralleling as closely as possible the conditions existing in a regular softening system, even allowing more time for the reactions and with the aid of heat.

The time factor for the treatment of a particular water supply cannot therefore be directly determined by laboratory experiment, but must be found by a comparison of the experimental data with the results in practice.

The presence or absence of certain salts seems to have a direct bearing upon the time required for reactions and upon the solubilities of the calcium and magnesium compounds remaining in the treated water; but so far, no reliable data are available that would warrant stating an opinion as to which of these salts cause this variation; nevertheless, the fact re-

mains that the calcium and magnesium cannot be reduced to the same limits in all waters.

In some waters, at atmospheric temperature, the reactions are completed and the water has settled perfectly clear at the end of two hours. In other waters, under the same conditions, and with the same type of apparatus, this result is not obtained until at the end of eight hours, and in some cases even a longer time. Therefore, in practice the time to be allowed is an important consideration, since the cost, as well as the extent of the softening, is dependent upon the time allowance for reactions and sedimentation.

Each water presents a specific problem that has to be worked out from the analysis, the experimental data, and the known results in practice with water of similar characteristics. In the absence of such data neither the results to be obtained can be accurately foretold, nor troubles avoided that follow imperfect softening.

It is, of course, true that any softening of the water is better than none, but by carefully considering the important factors which enter into the design of a water-softening system for a particular water supply, the additional outlay will be well invested, as there is a vast difference between the extent of softening obtained in many plants, due to improper design, and that which is obtainable with properly designed and operated apparatus.

THE FOREST PRODUCTS LABORATORY.

By MCGARVEY CLINE, DIRECTOR.

What It Is.—The Forest Products Laboratory is a laboratory of practical research conducted by the Forest Service, United States Department of Agriculture, in coöperation with the University of Wisconsin. The purpose of the laboratory is:

1. To secure authoritative information on the characteristic mechanical and physical properties of commercial woods and products secured from them.

2. To study and develop the fundamental principles underlying the preservative treatment of wood, its use for the production of fiber products (pulp, paper, fiber board, etc.), and its use in the manufacture of alcohol, turpentine, rosin, tar and other chemical products.

3. To develop practical ways and means of using wood which, under present conditions, is being wasted.

4. To serve as a public bureau of information on the properties and utilization of forest products.

5. To coöperate with consumers of forest products in improving present methods of use; also in formulating specifications and grading rules for commercial woods, materials secured from them (gums, oils, resin, etc.), and materials used in the treatment of wood (creosote, zinc chloride and other preservatives).

The laboratory is at Madison, Wisconsin, and is situated on the northwest corner of Randall Field, the athletic field of the University of Wisconsin. The university furnishes, without cost to the Forest Ser-



Fig. 1.—Forest Products Laboratory. Front and side view.



Fig. 2.—Forest Products Laboratory Storage Yards and rear view of building.

vice, the building, grounds and the heat, light and power required for the operation of the laboratory. The Forest Service employs the entire staff, supplies all equipment, and pays all other operating expenses. The equipment is available to the faculty and students of the university for research purposes only,

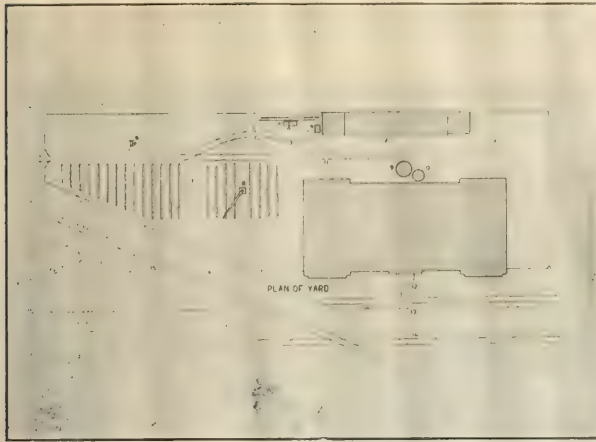


Fig. 3.—Plan of buildings and storage yard.

Legend: 1. Closed sheds for storage. 2. Open sheds for air-drying wood. 3. Sawmill. 4. Small circular saw. 5. Large circular saw with log carriage and direct connected motor. 6. Xylometer for measuring volume of ties. 7. Skids for piling logs and lumber. 8. Derrick. 9. Storage tank for preservatives, having carload capacity. 10. Auxiliary storage tank for preservatives. 11. Switch from C. M. & St. P. Ry. 12. Sidewalk. 13. Curb line, University Avenue. 14. Street car track. 15. Railroad track, C. M. & St. P. Ry.

and the laboratory staff presents a course of lectures at the university on the commercial uses of the forest resources of the country.

Its Field of Work.—The following summary of the kinds of work conducted at the laboratory will give the reader a fairly comprehensive idea of its field of work:

1. Physical characteristics of wood:

The physical properties of woods studied are its specific gravity, shrinkage, microscopic structure,

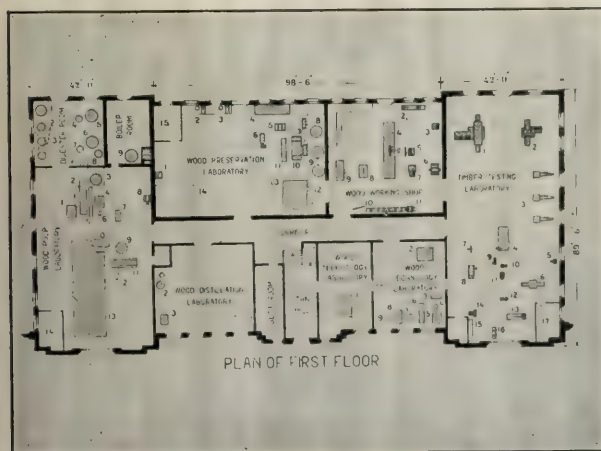


Fig. 4.—Forest Products Laboratory. Plan of first floor, showing location of principal pieces of apparatus.

Legend: Wood Technology Laboratory—1. Work bench. 2. Apparatus for testing beams under dead load. 3. Vacuum oven. 4. Carbon dioxide generator. 5. Motor-driven air compressor. 6. Condenser and

humidifier. 7. Small automobile boiler, for inside of cylinder. 8. Wood conditioning cylinder. 9. Small automobile boiler for cylinder jacket.

Wood Pulp Laboratory—1. Drum washer. 2. 6 Plate screen. 3. Stock tank. 4. Drum washer. 5. Riffler and sand settler. 6. Stuff pump. 7. Power press. 8. Power motor. 9. Stuff chest. 10. Machine screen. 11. Beating engine. 12. Stuff pump. 13. "Pusey Jones" paper machine. 14. Office.

Digester and Boiler Rooms—1. Alkali storage tank. 2. "Acid" making system. 3. Acid pumps. 4. Soda digester. 5. Soda blow pit. 6. Sulphite blow pit. 7. Sulphite digester. 8. Relief liquor tank. 9. 10 H. P. boiler.

Wood Distillation Laboratory—1. Condenser. 2. Steam distillation retort. 3. Destructive distillation retort. 4. Turpentine refining still.

Wood Preservation Laboratory—1. Regulating device for controlling the amount and temperature of water for fungus pit. 2. 12" dia. x 24" pressure cylinder; maximum working pressure 300 lbs. per sq. in. 3. 8" dia. x 12" pressure cylinder with pressure pump; maximum working pressure 300 lbs. per sq. in. 4. Concrete open tank. 5. 18" dia. x 4 ft. pressure cylinder; maximum working pressure 600 lbs. per sq. in. 6. Motor-driven centrifugal circulating pump. 7. 300 lbs. to 600 lbs. pressure pump (hydraulic). 8. Compressed air receiver. 9. Measuring tanks. 10. 3.5' x 12' pressure cylinder; maximum working pressure 300 lbs. per sq. in. equipped with treating car. 11. Vacuum pump with surface condensers. 12. Sump. 13. Platform treating car scales. 14. Fungus pit. 15. Office.

(Left out)—Wood penetrance apparatus. Hot well. Air compressor. (In pit below floor)—Two receiving tanks. Two tanks for concentrated zinc chloride.

Wood Working Shop—1. Work bench. 2. Wood turning lathe. 3. Mortiser. 4. Short log saw mill and edger. 5. Trimmer. 6. Surfacers. 7. Band saw. 8. Circular saw. 9. Jointer. 10. Cut-off saw. 11. Power motor.

Timber Testing Laboratory—1. 200,000 lbs. Richlé testing machine. 2. 100,000 lbs. Olsen testing machine. 3. 30,000 lbs. Olsen testing machine. 4. Torsion testing machine. 5. Power motor. 6. Impact testing machine. 7. Grindstone. 8. Shaper. 9. Hack saw. 10. Large drill press. 11. Small drill press. 12. Emery wheel. 13. Machine lathe. 14. Milling machine. 15. Work bench. 16. Gas furnace. 17. Office.

(Left out)—Bench drill press. Revett precision lathe. Drill grinder.

and, in the case of some species, its specific heat and heat conductivity. Data secured from investigations of this class are chiefly used in correlating the results of other experiments.

2. Mechanical properties of wood:

The term "mechanical properties" as used in the laboratory is applied to those properties of wood which enable it to resist the action of mechanical

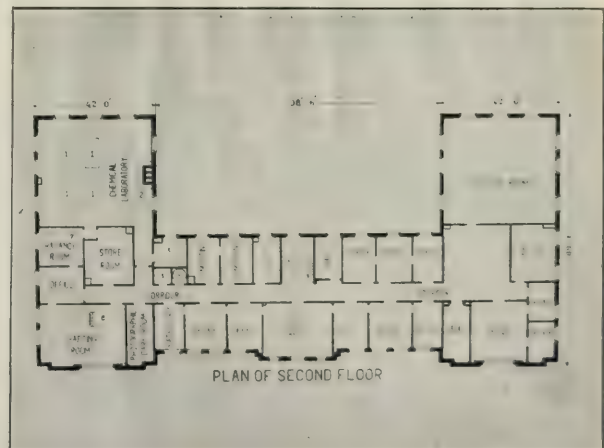


Fig. 5.—Forest Products Laboratory.—Plan of second floor, showing arrangement of offices and laboratories.

Legend: 1. Work benches. 2. Hoods. 3. Distillation room with work benches. 4. Elevator. 5. Spiral stairway to attic. 6. Blue-printing machine. 7. Bench for balances.

forces. Strength, stiffness, hardness, and toughness are examples of such properties. This work includes tests on small clear specimens free from defects, structural timbers, and manufactured forms such as

spokes, axles, etc. Tests are also made to determine the effect of methods of seasoning, preserving, and fire-proofing on the mechanical properties. The chief purpose of work of this character is to furnish engineers and architects data upon which to base moduli for design and upon which to base commercial specifications; to permit manufacturers using wood to judge the desirability of substituting other woods for those becoming scarce; and to determine how

5. Agencies destructive to wood:

A branch of the Office of Forest Pathology of the Bureau of Plant Industry is located at the laboratory for the purpose of studying wood-destroying fungi and how they are affected by various wood preservatives. The chief purpose of this work is to suggest ways and means of perfecting the preservative treatment of wood. The laboratory also coöperates with the Bureau of Entomology in studying insects



Fig. 6.—Timber Testing Laboratory, showing 30,000 lbs. universal testing machine in the foreground and machine shop equipment in the background.

wood can be seasoned and treated with the least injury to its strength.

3. Chemical characteristics and properties of wood:

This work consists of experiments to determine the quantity and quality of essential oils, tannins, gums and other products which may be secured from different woods. It bears directly on the practicability of using certain forms of forest waste.

4. Artificial drying of wood:

This class of work includes the study of commercial dry-kilns and their operation; also the experimental study of different methods of drying wood. The proper seasoning of wood is a most important factor in its use, and one which is at present too frequently neglected.

and other animal organisms which destroy wood.

6. Wood preservation:

This division of work includes all problems dealing with the impregnation of wood with preservatives, fire-proofing substances and other materials. At present its attention is largely directed to the study of preservatives and preserving processes. Wood preservation concerns principally the railroads, mines and other large consumers of structural timbers, but it also is of much interest to the building trades and to municipalities interested in wood as a paving material.

7. Wood distillation:

This line of activity is directed to the study of methods of distilling wood and methods of refining

and grading the products secured. Work is also done to demonstrate the practicability of using certain of the products for different purposes, thus creating a market for them. This work bears directly on the possibility of using the enormous quantities of mill and forest waste.

8. Pulp and paper industries:

The pulp and paper work of the laboratory is confined to the study of the use of different species and forms of wood for the production of pulp and paper products. The chief purposes of the work are to determine the value, for the production of pulp, of

and result in much unnecessary damage to the standing timber, and cause an unnecessary loss in value of the turpentine and rosin produced. The purpose of the work conducted by the laboratory is to improve this situation.

Its Organization and Equipment.—The laboratory is divided into the following nine sections:

- Maintenance.
- Engineering.
- Timber Tests.
- Wood Preservation.
- Wood Technology.

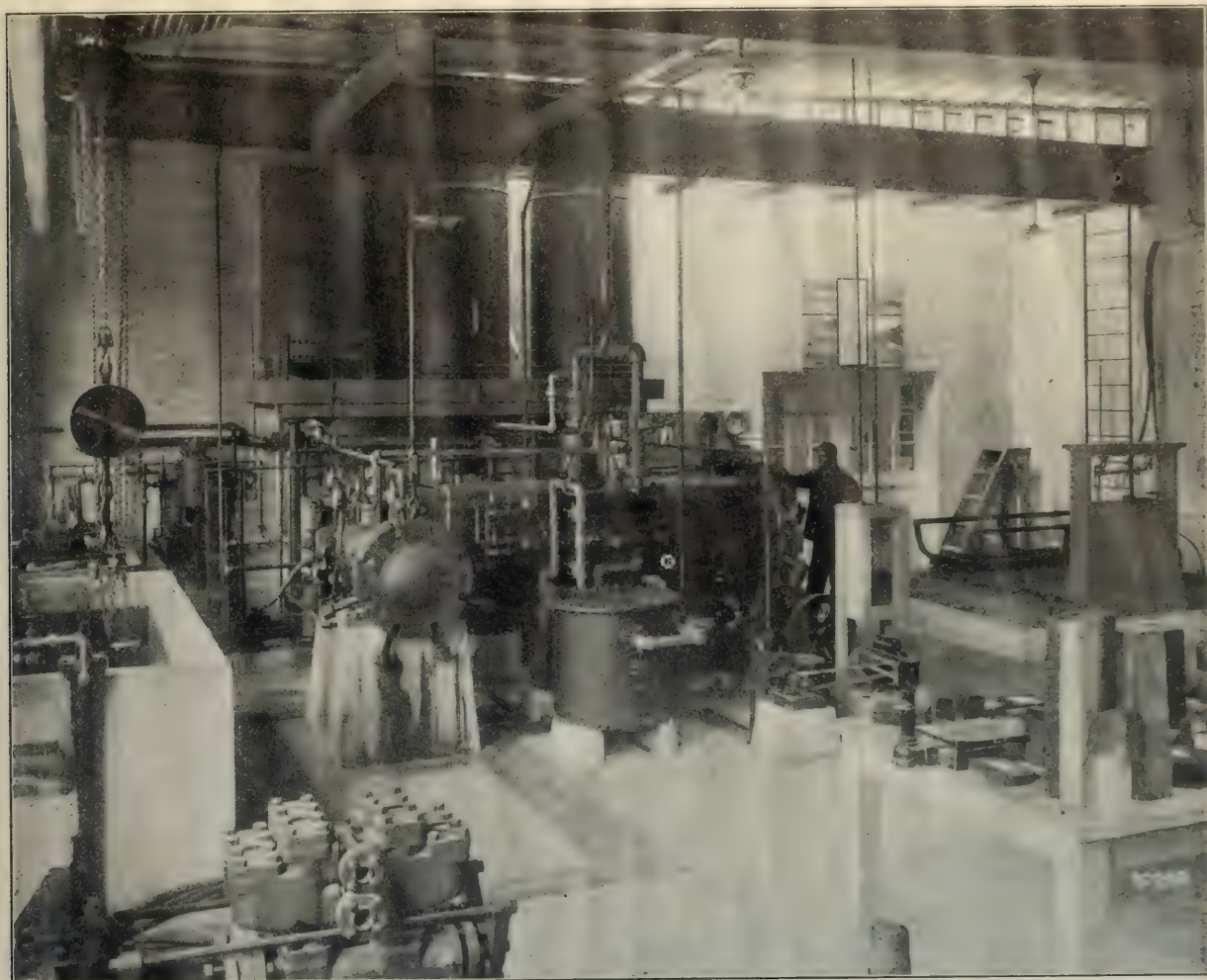


Fig. 7.—Wood Preservation Laboratory, showing experimental cylinders and measuring tanks.

woods not being used at present, and to conduct experiments for the purpose of perfecting present methods of manufacturing wood pulp. Especial attention will be given in this work to the development of methods of manufacturing a commercial pulp from wood which is at present being wasted.

9. Production of naval stores:

Methods employed in the production of turpentine and rosin are also studied by the laboratory. Work of this character is confined to the chipping of the trees, the collection of the gum, and the distillation of the resin secured. The present methods employed in the production of naval stores are crude

Wood Distillation.

Pulp and Paper.

Chemistry.

Pathology.

These sections are responsible to the Director and to two Assistant Directors.

Figs. 3, 4, and 5 show the general arrangement of the laboratory and the storage yards; also the location of the different section laboratories and the arrangement of the offices. The descriptive keys dealing with each of these figures list the equipment of the different sections.

Maintenance.—The section of Maintenance is

charged with the general up-keep of the building and the purchase of all supplies and equipment. It also supervises the force maintained for handling computing work of a routine character and the section of stenography. It also has charge of the library and file room and the indexing and filing of all laboratory records.

Engineering.—The section of Engineering has charge of the storage yards, the sawmill, the wood shop, machine shop, and drafting-room. It is charged with the care of all materials stored in the yard, the design and repair of apparatus. Its work, however,

from the forests, and include the study of all the mechanical properties which determine the suitability of wood for different uses.

2. Tests to determine the effect of mechanical operative features of pressure wood-preserving plants on the strength of wood.

3. Tests to determine the mechanical efficiency of joints and fastenings used in wooden structures.

Wood Preservation.—The section of Wood Preservation studies the problems confronting the wood-preserving industry. These problems may be broadly classified into:

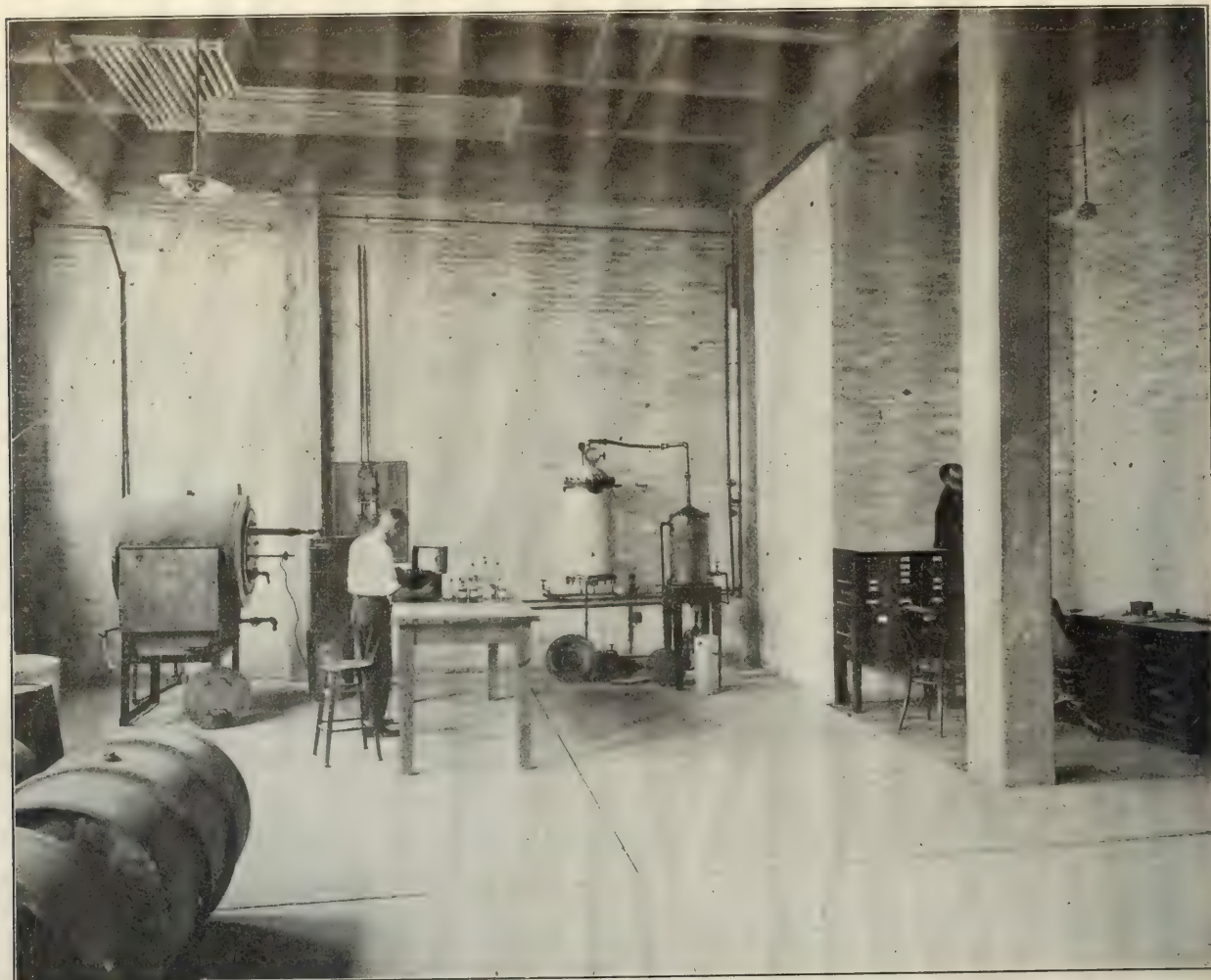


Fig. 8.—Wood Distillation Laboratory, showing experimental retorts for steam and destructive distillation.

is conducted in collaboration with the other sections of the laboratory.

Timber Tests.—Fig. 6 shows a general view of the timber-testing laboratory. This section conducts all tests to determine the mechanical properties of natural or treated wood. The following series of tests, which are under way at present, is representative of those conducted in the laboratory:

1. Tests to determine the relative mechanical properties of the commercial woods of the United States.

These tests are being made upon material secured

a. Those dealing with the preservatives themselves.

b. Those dealing with the methods of getting the preservatives into the woods.

To study the first class of problems, the laboratory is provided with a fungus pit which contains chambers thoroughly inoculated with various wood-destroying fungi. The humidity and temperature of the pit will be so regulated that conditions in it will be most favorable to the growth of fungi. Wood will be treated with different preservatives and placed in the pit. The efficiency of the preservative will be

determined by its ability to resist the fungi. In addition to such laboratory experiments, timbers are treated and placed in actual service and are carefully inspected at periodic intervals.

The second class of problems are primarily problems of mechanical engineering, dealing with the methods of forcing the required amounts of various preservatives into the different species and forms of wood. The laboratory is well equipped for studying any of the processes used for the preservative treatment of wood. Fig. 7 gives a general view of the laboratory. The storage tank in the yard is

track will be inspected and its condition reported from year to year by the staff of the laboratory.

2. The fungicidal properties of coal-tar creosote fractions.

These experiments are for the purpose of determining the relative efficiency of different fractions of coal-tar creosote in preventing decay. Specimens treated with the different fractions are also being placed in the waters of the Gulf of Mexico and the Bay of San Francisco to determine the relative efficiency of the different fractions in protecting yellow pine from marine bearers.

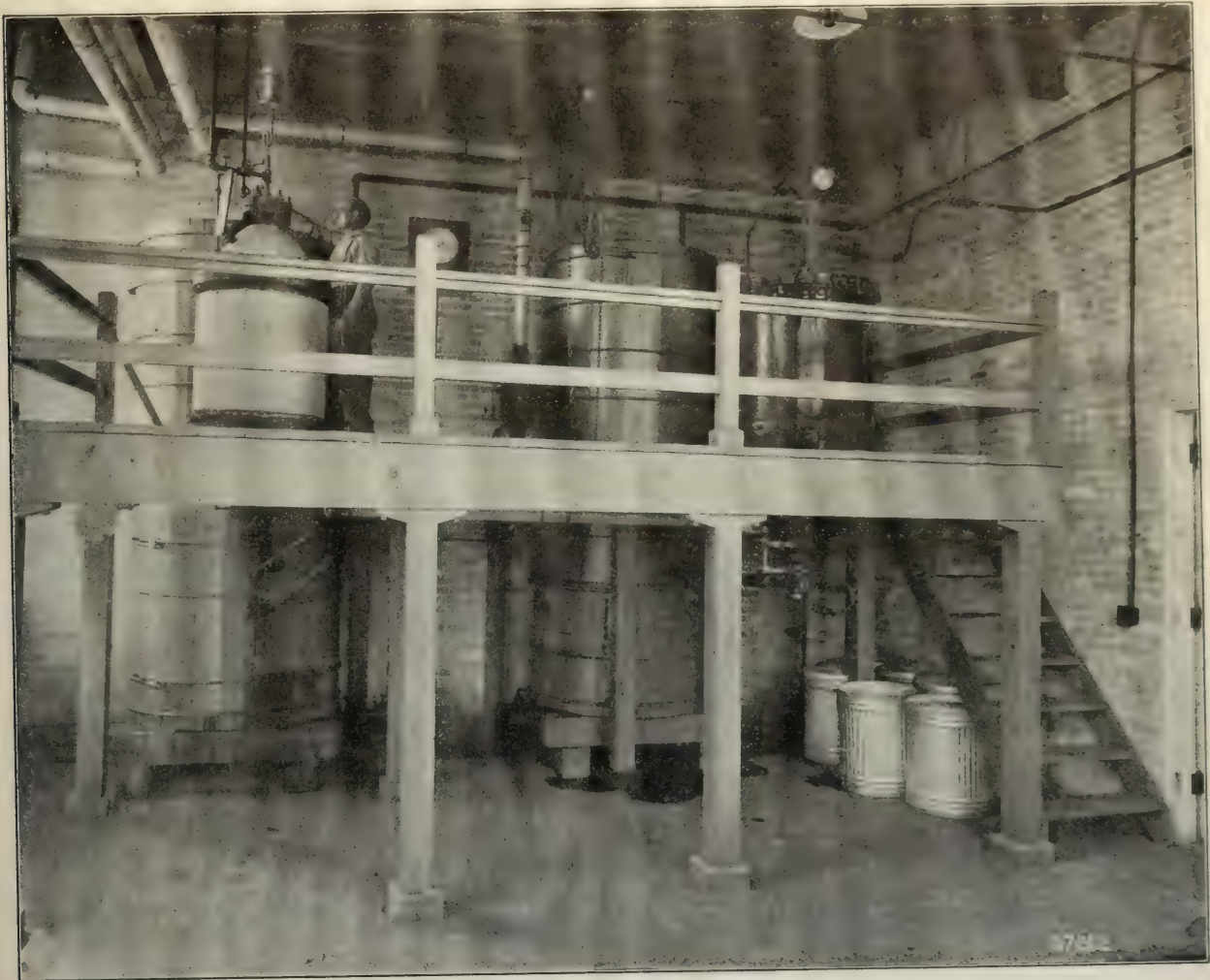


Fig. 9.—Digester Room, Pulp and Paper Laboratory, showing soda and sulphite digesters and blow pits.

sufficient in size to provide for a carload of any preservative. The general arrangement of the equipment of this laboratory may be seen by referring to Fig. 4. Typical projects at present under way are:

1. Service tests on red oak and maple cross ties, in coöperation with the Chicago, Milwaukee & St. Paul Railway Company, to determine the relative efficiency of standard preservatives and processes.

This work calls for the preservative treatment of approximately 1600 red oak and maple cross ties, which, after treatment, will be placed in a test track by the Chicago, Milwaukee & St. Paul Railway. The

3. The preservation of timbers used in the construction of silos.

Wood Technology.—In addition to the equipment shown on the laboratory plan, this section is provided with microscopes, microtomes, and other apparatus required for the study of wood structure. It is also equipped with taking photomicrographs. Work at present under way includes:

1. The correlation of microscopic structure of commercial woods with their properties and uses.
2. Temperature changes in wood under treatment. These experiments are designed principally to de-

termine the rapidity with which wood may be heated under different conditions.

3. The analytical study of artificial methods of drying wood.

These experiments will be conducted in an especially designed, steam-jacketed cylinder which is so connected with air pumps and sources of steam supply that a great variety of conditions can be secured.

Distillation.—Fig. 8 shows a general view of the distillation laboratory. This laboratory is at present equipped for studying both steam and destructive distillation processes. It is also equipped with a

c. Refining of the crude products.

At the present time the energies of the section are directed entirely to the study of resinous woods. The woods being first investigated are southern pine and Douglas fir.

Pulp and Paper.—Fig. 9 shows the experimental digesters and blow pits, while Fig. 10 shows the 15-inch Fourdrinier paper machine, and, in the background, washers, screens and other equipment of the laboratory. In addition to the equipment shown on the plans of the pulp and paper laboratory, the Forest Products Laboratory has just completed the installa-

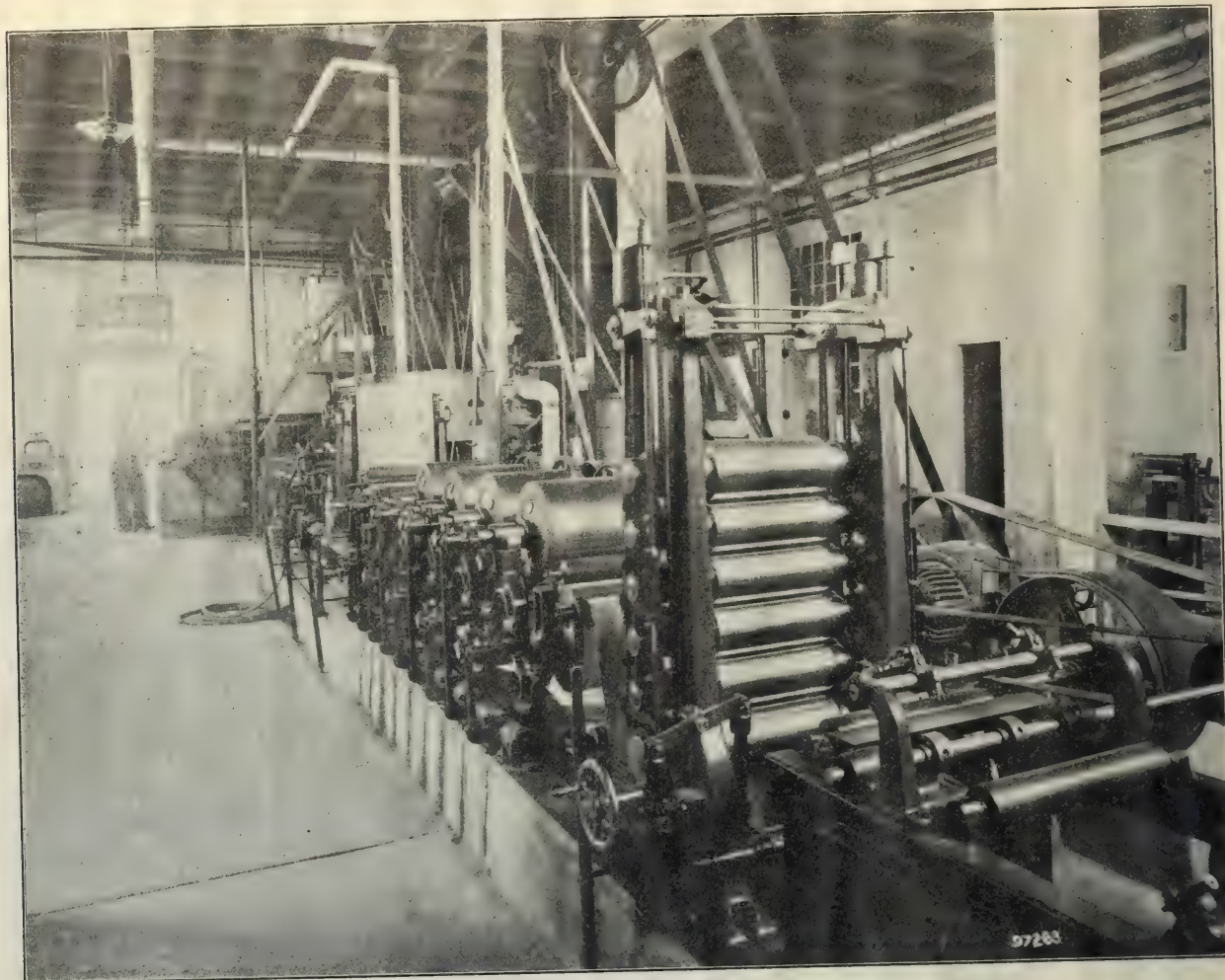


Fig. 10.—Pulp and Paper Laboratory, showing Fourdrinier paper machine, and, in the background, washers, screens, and other equipment.

fractionating column still which, at this time, is set up at the plant of the Atlantic Turpentine Company at Mount Pleasant, Georgia, where experiments are being conducted with it to determine the best method of commercially refining wood turpentine. The still is of such a capacity that materials can be handled on a commercial scale. The work of this section naturally divides itself into:

a. Experiments to determine what products and how much of them can be secured from different woods.

b. The design and operation of machinery best adapted to the production of those products having the greatest value.

tion of a ground-wood laboratory at Wausau, Wisconsin. The laboratory at Wausau is equipped with a heavy-duty commercial grinder connected with a 500 horse-power motor-generator set. It also contains screens, a wet machine, a barker, and other equipment necessary for the commercial manufacture of ground-wood pulp. The plant is so designed that the speed of the grinder can be varied through wide limits. Its chief purpose is to determine whether commercial ground-wood pulp can be made from woods other than spruce. The work at Wausau is being conducted under a special appropriation.

Chemistry.—Figs. 11 and 5 show the general arrange-

ment of the chemical laboratory and its equipment. The work of the section of Chemistry is largely to supplement the work of the other laboratories. Its purposes are:

a. To find uses for products at present having little or no commercial value.

b. To secure data upon which to base commercial specifications for wood products, wood preservatives, and other chemical problems that come up in connection with the work of the other sections.

Typical projects are:

i. The classification of commercial creosotes according to their chemical and physical properties.

treated in every respect as a member of the laboratory staff. An extensive collection of wood-destroying fungi is being made and cultures of them are being propagated in the fungus pit of the wood-preserving laboratory. The section of Pathology coöperates with the laboratory in conducting this class of work.

How It Works—Internal Relations.—The preceding part of this paper, it is hoped, has given the reader a fair conception of the purpose of the laboratory, its field of work, and its material resources. Its success, however, must depend largely upon the personnel of the organization and upon the ability of the different men composing it to work together in a manner

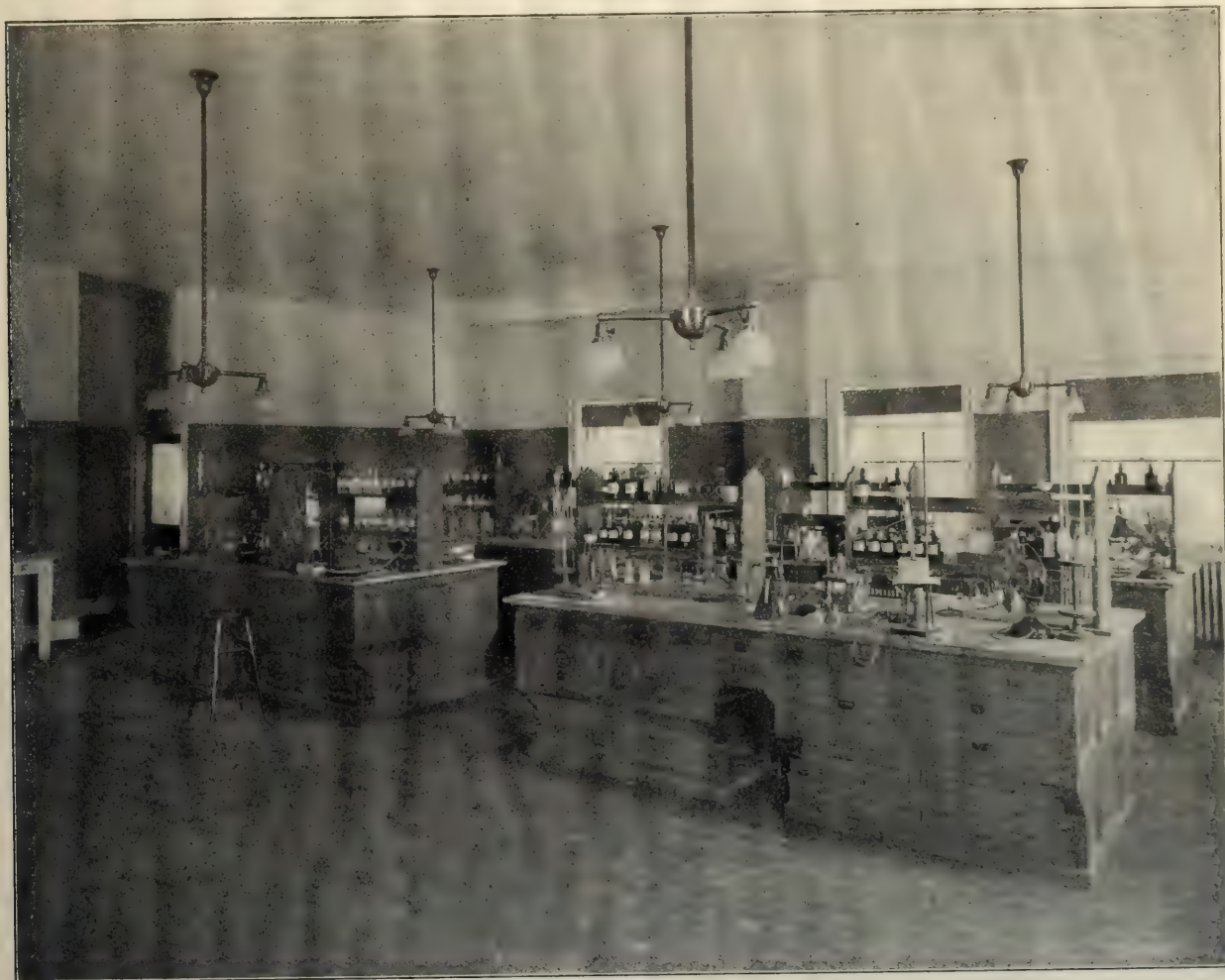


Fig. 11.—Chemical Laboratory.

2. Experiments to determine the quantity and quality of tannin in various kinds of wood and bark.

3. Methods of analyzing treated wood to determine the kind and quantity of preservative in it.

Pathology.—As previously stated, the section of Pathology is not, correctly speaking, a section of the Forest Products Laboratory, since its work is under the direction of the Bureau of Plant Industry. The man detailed to the laboratory, however, gives his full time to the study of pathological problems bearing on the use of wood. The Forest Products Laboratory supplies him with facilities for work and he is

which will insure coöperation on the part of the different sections and the proper coördination of their work.

The entire staff of the laboratory, consisting of approximately sixty people, is employed in accordance with the regulations of the United States Civil Service Commission. The men are recruited from the professions of engineering, chemistry, forestry, and pathology, also from the different grades of clerks and skilled laborers. A large percentage of the staff are young and comparatively inexperienced, this condition being due chiefly to the newness of the

work and to the loss of experienced men to commercial interests. It is therefore necessary to have the staff so organized that new material will be trained as soon as possible by the more experienced men of the organization, and that plans of work and records of experiments shall be made and kept in such a way that, with a reasonable amount of study, the work of any man can be taken up and completed by another with the least loss of time and money. With this in view, the following principles are closely adhered to:

1. Each investigator must have a clear conception of the purpose and value of his investigation and the methods which he intends to follow in conducting it, and that he make such conceptions and methods a matter of record.

2. The plans for conducting investigations should be perfected, so far as possible, before work is actually begun.

3. That all pertinent information on the materials used in the experiments, should be secured and recorded.

4. That in the different sections standard methods and terms be used, so far as possible, in order that the work of the laboratory may be coördinated to the best of advantage.

5. That frequent partial summaries and analyses of results be made so that plans may be modified, if necessary, before the work has proceeded too far.

6. That final and complete summaries and analyses of results be embodied in a report which shall be a permanent record of the work.

To facilitate the application of these principles, and to insure the publication of results as soon as possible, the experimental work of the laboratory is classified into projects. A project may consist of a series of tests or experiments conducted

- (a) For the purpose of investigating some specific problem on experimental research;

- (b) To verify experimental results on a commercial scale;

- (c) To assist outside parties in the application of scientific principles and processes of recognized commercial value with which the laboratory is familiar.

Projects may be conducted independently by the laboratory or in coöperation with an individual or commercial or other organization.

Each project is assigned to a member of the staff who is responsible for taking the initiative in all matters pertaining to it. In general, such an assignment involves:

1. A preliminary investigation: This work embraces a review of literature and results which have been secured by previous investigators, also frequently tentative experiments to ascertain the best methods of attacking a problem. The results of a preliminary investigation are summarized in a written report, which sometimes is made the basis of a publication.

2. Working plan: If the preliminary investigation shows the need of further work, a working plan is prepared. This plan records the purpose of the work, gives instructions for collection of material

required and the methods which it is proposed to follow in conducting the work.

3. Description of material: If the working plan is approved, the materials called for are secured and a record made of their origin and history.

4. Progress reports: From time to time as work on a project progresses, the man in charge of it prepares project reports containing summaries and analyses of results secured, in order to determine whether it is necessary to make modifications in the working plan.

5. Project report: When all the data called for by any plan are obtained, the man in charge of a project prepares a final report, giving a full discussion of results and conclusions reached. Project reports are the bases for most of the circulars and bulletins published by the Department, dealing with the work of the laboratory.

In order to give the fullest opportunity for constructive criticism, all working plans are submitted to one of the technical committees with which the staff is organized, each committee being composed of the members of the staff most experienced in the lines of work referred to it for consideration. Committee work of this character has precedence over all other work of the laboratory. After review by the committee, to give further opportunity for constructive criticism, and to keep the different members of the staff informed on all of the work of the laboratory, working plans are presented and discussed at the general staff meetings which are held each Saturday. All men in charge of important lines of work attend the general staff meetings. After full opportunity has been given for discussion, all plans are submitted to a committee composed of the director and two assistant directors for approval. Results of preliminary investigation, progress on various projects, inspection trips, and other matters of general and technical interest are discussed at the staff meetings.

Once a month seminar meetings, open to the entire technical staff of the laboratory, are held, at which the technical literature relating to the work of the laboratory is reviewed, and technical papers are presented.

Relations to Societies and Associations.—It is the constant aim of the laboratory to relate itself closely to the activities of societies and associations interested in its work, and to make such relations of mutual advantage. With this in view, members of the staff are encouraged to become members of the organizations of this character in which they are most interested, and when they are honored by committee assignments, it is the policy of the laboratory to do everything possible in making such service of value to the society or association and a credit to the Forest Service. Such coöperation is not limited to the organizations represented on the laboratory staff, but is extended to all societies and associations which may wish to use the resources of the laboratory.

Relation to Individuals and Commercial Organizations.—As stated in the first pages of this paper, one of the chief purposes of the Forest Products Lab-

oratory is to serve as a public bureau of information on the field of work which it covers, but it is not the policy of the Forest Service, aside from making available information which it has, to undertake work of any kind which is not of general interest to the lumbering or to one of the wood-using industries. It is frequently the case, however, that a problem confronting a commercial organization is one of general interest, and is also one in which the laboratory is interested. In such cases it is the policy of the Service to cooperate with the commercial organizations, the cooperating organization sharing the expense of the investigation in proportion to the direct benefits which result to it from the work done. Cooperation of this character varies from cases in which the coöperator merely furnishes a part of the material required for the work, to cases in which the entire expense of the work is borne by the cooperating company, the laboratory merely supplying the men to supervise the work. In all coöperative work of this character the Department of Agriculture reserves the right to first publish the results.

The possible value of the Forest Products Laboratory to the lumbering and wood-using industries will be readily recognized by all who are familiar with the problems confronting these industries. The actual value of the laboratory, however, depends upon its ability to obtain results of practical value. To secure such results to the best advantage it must have the support and coöperation of the men who are in constant and intimate association with commercial problems. The Service therefore invites such men to share with it the responsibility of making the Forest Products Laboratory play an important and useful part in reclaiming the wastes of the forests and in increasing efficiency in the commercial use of wood.

[CONTRIBUTION FROM THE LABORATORY OF SOIL FERTILITY INVESTIGATIONS.]

OXIDATION IN SOIL.¹

By M. X. SULLIVAN AND F. R. REID.

The advantage of aerating soils has long been known and is well recognized in the practice of tillage of the soil. Liebig² early pointed out the importance of a thorough aeration of soils. The phenomena of oxygen absorption by soils likewise early attracted attention. According to Liebig,³ Ingenhouss and DeSaussure found that vegetable mold extracted oxygen from air with great rapidity and replaced it by an equal volume of carbonic acid. Dehérain and Demoussy⁴ considerably later studied the process of oxygen absorption in several soils and found that oxygen was always taken up and carbon dioxide set free. In their method the soils were placed in a closed tube kept at constant temperature and after a certain time the gases were extracted and the carbon dioxide and oxygen determined. The carbon dioxide formed was taken as a measure of oxidation.

The oxidation was attributed by them to the action of microorganisms and to simple chemical action. Both kinds of oxidation increase with heat. Up to 65° C. the carbon dioxide increased. From 65° to 90° it decreased. Above 90° there was another increase in carbon dioxide. At 110° over six times as much carbon dioxide was formed as at 65° C. Some oxidation went on at 22° C. in soils which had been heated at 120° C. for one hour. Often more oxygen was consumed than could be accounted for in carbon dioxide formed.

Wollny¹ studied the rate of oxidation by determining the amount of carbon dioxide produced in a given time at a constant temperature. He concluded that the oxidation is due mainly to the activity of microorganisms. Lime favored oxidation. Chlorides and sulphates retarded while phosphates and nitrates favored.

More recently still Russell² studied oxidation by estimating the oxygen absorbed by soils. He found that the same factors which influence fertility also influence the rate of oxidation and apparently to the same extent, that oxidation was greater in fertile soils than in infertile soils, in surface soil than in subsoil. With different soils of the same type the rate of oxidation varies in the same way as the fertility and may be used to measure it. Pasture soils, however, are excluded. Russell suggests that the oxygen absorbed measures the total action of microorganisms which by producing enzymes, etc., hasten decomposition.

As shown by Russell, the assumption that the evolution of carbon dioxide is proportional to the amount of oxygen absorbed is not proved. Many soils, as is well known, have a great power of absorbing carbon dioxide. Russell's method of measuring the amount of oxygen absorbed is a very good method, but requires a somewhat complex apparatus, takes considerable time to show differences in soils and marks respiration of microorganisms as much as oxidative changes in the soil constituents. A simpler test of oxidative processes in soils we have found in the changes produced in easily oxidizable substances brought in contact with the soil, such as aloin, pyrogallol, hydroquinone, paraphenylenediamine, benzidine, guaiac, *α*-naphthylamine, which speedily show oxidative processes and have been used extensively as a test of such processes. By means of these easily oxidizable chromogenic substances the plant roots have been shown to have a strong oxidative power.³ This power was found to be affected by agencies which affected soil fertility, such as fertilizer salts, toxic substances, etc., and was shown to have a considerable agricultural interest in that it could affect alteration in the soil constituents and thus influence soil fertility, especially in connection with fertilizers and a system of crop rotation. Microorganisms which abound in soil likewise have been found capable of bringing about powerful oxidation

¹ Published by permission of the Secretary of Agriculture.

² Liebig's "Complete Works on Chemistry," p. 44, 1852.

³ *Ibid.*, p. 113.

⁴ *Ann. Agron.*, 22, 305 (1896).

¹ "Die Zersetzung der organ. Stoffe. und die Humusbildungen," Heidelberg, 1897.

² *Jour. Agric. Sci.*, 1, 261 (1905-6).

³ Schreiner and Reid, *Bot. Gaz.*, 47, 355 (1909).

of substances in the medium in which they grow.

The oxidizing principles, be they enzymes or other bodies, were found in water in which the roots of growing seedlings had stood for twenty-four hours. Woods¹ has reported that the oxidizing enzymes may remain in soil for a considerable time. So it should be expected that, by the disintegration of microorganisms and plant roots, the material which brings about oxidation should be left in soil. In addition the soil *per se* should have, *a priori*, an oxidizing power due to inorganic oxygen carriers like salts of iron and manganese and probably to organic matter in an unstable, highly oxygenated state analogous to quinone, benzaldehyde, terpene bodies, or organic peroxides, which might readily give up oxygen in an active state or activate the oxygen of the air.

In passing, it may be said that absorption of oxygen by a soil and the oxidation of readily oxidizable substances, such as the chromogens mentioned, by the soil are not necessarily the same phenomenon. In fact, the two methods might be employed together with advantage in the study of different phases of soil oxidation.

Of the reagents employed to test the oxidizing power of the soil, a water solution of aloin was found to be best. The results with this and various other reagents are given in the following table:

TABLE I.—OXIDATION IN SOILS.

Soils.	Reagents.								
	Guaiac.	Guaiac + H ₂ O ₂ .	Aloin.	Aloin + H ₂ O ₂ .	Hydroquinone.	Hydroquinone + H ₂ O ₂ .	Pyrogallol.	Pyrogallol + H ₂ O ₂ .	Paraphenylenediamine + H ₂ O ₂ .
1. Clarksville loam.....	+	++	+	+	+ sl	++	+	++	+
2. Takoma lawn soil.....	—	—	—	—	—	—	—	?	?
3. Marshall clay loam.....	—	—	—	—	—	—	—	?	?
4. Volusia silt loam.....	—	—	—	—	—	—	—	?	?
5. Arlington clay loam.....	+ sl	+ sl	+ sl	+ sl	—	—	+	+	?
6. Hagerstown loam in sod.....	+	++	+	+	+ sl	++	+	++	+
7. Hagerstown loam.....	+	++	+	+	—	+	+	++	+
8. Hagerstown loam + lime.....	+	++	+ sl	+	—	++	+ sl	++	+
9. Hagerstown loam + lime + manure.....	+	++	+ sl	+	—	++	+ sl	++	+
10. Hagerstown loam + complete fertilizer.....	+	++	+	+	—	+	+	++	+
11. Hagerstown loam + manure.....	+	++	+	+	—	?	+	++	+
12. Norfolk fine sandy loam.....	—	—	—	—	—	—	—	—	—
13. Cecil fine sandy loam.....	—	—	—	—	—	+	+	—	?
14. Leonardtown loam.....	—	—	—	—	—	—	—	—	—
15. Dekalb silt loam.....	+	+	+	+	—	+ sl	+	+	+
16. Duchess silt loam.....	—	—	—	—	—	—	—	—	—
17. Sassafras silt loam.....	+ sl	+ sl	+ sl	+ sl	—	—	—	—	—
18. Orangeburg loam.....	+	+	+	+	—	+	+	+	+

In the experiments given in Table I, ten grams of soil were shaken in test tubes with 25 cc. of two per cent. alcoholic guaiac; 0.125 per cent. water aloin; 0.5 per cent. pyrogallol and hydroquinone. When hydrogen peroxide was added, it was to the extent of 0.5 cc. of a 3 per cent. solution to each tube. In case of testing with paraphenylenediamine, 25 cc. of a solution of a 2 per cent. solution of paraphenylenediamine plus 0.2 per cent. hydrogen peroxide, containing 1 cc. of concentrated sulphuric acid to the liter, were shaken with the soil. When oxidized the reagent develops a blue-black color. The control

solution oxidized so readily, however, that it was not considered a good medium for testing oxidation and was regarded as too sensitive for differential work.

As regards the significance of the oxidation as given in the preceding pages, it may be said that soils known to have good productive power had strong oxidative power, as a rule, and that the poorer soils had little or no oxidative power. The oxidative power and productivity, however, do not necessarily agree, since we have found soils of slight oxidative power which have given the better growth as compared with soils of stronger oxidizing power. Crop production, as is well known, is dependent upon many factors, no one of which can be taken as an absolute criterion. As will be shown later, however, certain factors which favor productiveness of soils favor oxidation, so the study of oxidation in soil has considerable value in relation to soil fertility.

METHOD OF TESTING OXIDATION IN SOIL.

Since aloin dissolved in water proved to be the best medium for testing oxidation, a water solution of aloin, generally of a strength of 0.125 per cent., was employed in the further study of oxidation in soil. As a rule, 20 grams of soil were shaken four or five times in the course of an hour with 50 cc. of the aloin solution and allowed to settle; then the mixture

was treated with 50 cc. of 95 per cent. alcohol to flocculate the soil and to extract the oxidized aloin. If the oxidized aloin solution was fairly clear, the alcohol was dispensed with. The solution was then centrifuged, the supernatant liquid poured off and the depth of color in the solution compared by means of a colorimeter. The experiments from the time of adding the aloin to the soil to the reading in the colorimeter ran, as a rule, from two to three hours.

EFFECT OF VARIOUS TREATMENTS ON SOIL OXIDATION.

Poisons and Antiseptics.—Reducing agents like hydroxylamine hydrochloride, oxalic acid, sodium

¹ *Centralbl. f. Bakt.*, II, 5, 745 (1899).

thiosulphate, and formalin totally check the oxidation by soils. Mercuric chloride, silver nitrate, and carbon bisulphide had little retarding action on the oxidation and sometimes even increased it, though of themselves these antienzymotic substances have no effect on aloin within the time of the experiment. Though the soil by its absorbing and combining powers renders toxic agents less effective than they would be in solution, the fact that oxidation goes on in the presence of comparatively strong solutions of mercuric chloride, 5 cc. of a 1 per cent. solution to 20 grams of soil, silver nitrate, 5 cc. of a 1 per cent. solution to 20 grams of soil, and carbon bisulphide, 2 cc. of a 100 per cent. solution to 20 grams of soil, would indicate, contrary to our expectation, that little if any of the oxidizing action of the soils tested can be attributed to enzymes, though in other soils or under other conditions it may be possible that the oxidizing enzymes play a considerable rôle.

Dry Heat.—Several soils which showed a strong oxidation toward aloin were heated one and one-half hours at 105° C. dry heat and after cooling were shaken with the aloin solution. The oxidation of the aloin was reduced considerably by heating in the case of most of the soils tested. In some cases, especially in the Hagerstown loam, the heated soils gave such a different shade of color with so much of the original yellow of the aloin solution, that their oxidative power could not be compared accurately with that of the normal soil. As read by means of the colorimeter, the comparative oxidation was judged to be as follows: Clarksville loam, unheated 100, heated 100; Orangeburg loam, unheated 100, heated 111; Sassafras silt loam, unheated 100, heated no oxidation; Arlington clay loam, unheated 100 (slight), heated no oxidation; Hagerstown loam, unheated 100, heated 66; Hagerstown loam (manured), unheated 100, heated 45; Hagerstown loam plus complete fertilizers, unheated 100, heated 66.

Steam Heat.—Heating the soils for one and two hours, respectively, in an Arnold steam sterilizer lessened oxidation in most soils but had no retarding effect on Orangeburg loam. The relative oxidations of the unsteamed and steamed soils are given in the following table:

TABLE II.—EFFECT OF STEAM HEAT ON THE OXIDATIVE POWER OF SOILS.

	Unsteamed.	Steamed 1 hour.	Steamed 2 hours.
Hagerstown loam.....	100	65	faint
Hagerstown loam manured....	100	52	faint
Hagerstown loam plus complete fertilizer.....	100	34	faint
Sassafras silt loam.....	100 sl	neg.	neg.
Arlington clay loam.....	100 sl	neg.	neg.
Clarksville silt loam.....	100	54	faint
Orangeburg loam.....	100	104	105

Heat is a more effective inhibitor of the oxidative power of the soil than are the powerful anti-enzymotic substances such as mercuric chloride, silver nitrate, and carbon bisulphide. As compared to heat, these reagents retard oxidation but little and in some soils silver nitrate and carbon bisulphide even increase oxidation. Accordingly it is to be judged that the effect of heat on oxidation by soils

is due to its effect on the soil ingredients and especially on the organic matter or some inorganic-organic complexes of the soil since steam heating for two hours would affect strictly inorganic salts destructively but little, if at all. The organic matter of the soil, however, is known to undergo considerable modification at the temperature of 100° C.¹

Incineration.—When various soils which had a strong oxidative power toward aloin were incinerated the oxidative power was lost.

Acids on Incinerated Soils.—The addition of mineral acids such as hydrochloric and sulphuric had little effect in restoring the oxidative power of these soils. Acetic acid had a slight restoring effect. The organic hydroxyacids, on the other hand, greatly restored the oxidative power of the incinerated soils. Taking the Hagerstown loam plus acetic acid as 100, the comparative effect of the organic acids added to the incinerated soils is shown in the following table:

TABLE III.—EFFECT OF ORGANIC ACIDS ON THE OXIDATIVE POWER OF INCINERATED SOILS.

Soils.	Acetic.	Glycolic.	Malic.	Citric.
Hagerstown loam, manured.....	100	184	180	223
Hagerstown loam, complete fertilizer.....	100	184	180	223
Hagerstown loam.....	100	172	192	238

It would seem from the preceding table that the organic hydroxyacids are more effective in restoring the oxidative function of incinerated soils than are non-hydroxyacids or the mineral acids. Of the hydroxyacids tried, citric acid was the most effective in renewing the oxidative power of the incinerated soil.

Acids on Normal Soils. In a similar way the hydroxyacids added to normal soils tended to increase the oxidative power while related non-hydroxyacids had little effect on oxidation. Thus acetic acid slightly retarded or but little increased oxidation, while the related hydroxyacid, glycolic, increased oxidation to a great degree; succinic acid had little effect on oxidation or retarded it, while the related hydroxyacids, malic and tartaric, greatly increased oxidation; citraconic, itaconic, and mesaconic acids had little effect on oxidation in soil, while the related hydroxyacid, citric, greatly increased oxidation. Of the hydroxyacids, citric is somewhat the greater activator.

In some soils sodium citrate and tartrate were greater stimulators of oxidation than were equivalent quantities of the free acids. In every case, citric acid and sodium citrate increased oxidation more than tartaric acid or sodium tartrate. Dihydroxystearic acid slightly reduced oxidation in soil, while the potassium and calcium salts slightly increased it.

INFLUENCE OF VARIOUS SALTS WITH AND WITHOUT CERTAIN ORGANIC ACIDS AND THEIR SALTS.

Various salts of manganese, iron, aluminum, calcium, and magnesium have a greater or less oxidative action on a water solution of aloin. Accordingly, manganese in the form of the sulphate, chloride,

¹ See in this connection Lyon and Bizzell, *Bull.* 275, Cornell Univ. Agr. Exp. Sta. (1910).

carbonate and dioxide, iron as ferric chloride, aluminum as the oxide and the hydrate, calcium as carbonate, and magnesium as carbonate were added to various soils in the ratio of 100 parts of the metal to one million of soil, with and without the presence of organic acids and their salts. Manganese dioxide increased the oxidative power of the soils somewhat. All the other salts had little effect on the oxidative power of the soil, except in the presence of glycolic, tartaric, malic, and citric acids, and sodium citrate and tartrate. The best oxidation occurred in soils to which manganese and citric acid had been added.

Whether or not the oxidizing principle in the soil is manganese or other salts which are activated by the organic hydroxyacids in the incinerated soils and are rendered more effective in the normal soil, it seems most probable that the oxidizing power of the soil is due not to enzymes, but to a combination of inorganic constituents with definite kinds of organic matter. Since true enzymes readily undergo decomposition in solution, we should expect them to undergo decomposition readily in the soil.

INFLUENCE OF VARIOUS FACTORS IN SOIL OXIDATION.

Water Content.—The oxidation by the soils at optimum moisture is always considerably greater than that of the soils in air-dried condition.

Surface Soil Compared with Subsoil.—Of twenty-two soils which had more or less power to oxidize aloin, samples of the corresponding subsoils were tested. Of these subsoils, sixteen possessed no oxidizing power, three oxidized the aloin to a slight degree, two oxidized the aloin more than the soil did, and one equaled the oxidizing power of the soil.

Effect of Cropping.—The effect of cropping on soil oxidation is variable.

Effect of Fertilizing and Cropping.—To test the effect of fertilizing and cropping, wheat was planted in the various soils and allowed to grow for seventeen days. If the oxidative power of the fertilized and planted soil is determined immediately after the crop is removed, the planted soils tend to give a turbid solution and the comparative oxidizing power of the soils cannot be measured. If, however, the oxidative test be made ten to fifteen days after the crop was removed, the fertilized and planted soils show the greater oxidative power.

Effect of Fertilizers.—Numerous experiments have been made on the effect of fertilizers on the oxidative power of soils with results that show that the fertilizers sometimes increase oxidation, sometimes decrease it, and that the effects of the fertilizers are different in the different soils.

The action of the fertilizing salts must be attributed to the effect they have on the microorganisms of the soil, modifying their numbers and activities with a resulting modification of biochemical activities and a resulting change in both the amount and the condition of inorganic and organic soil constituents or directly on the soil constituents, especially in the organic matter which is undergoing change by auto-oxidation, or as a result of the activity of microorganisms. In short, the fertilizers added to soil or

present in soils do work and bring about various changes, one of which is made manifest by the changed oxidative power.

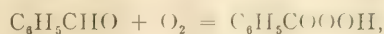
THE RELATION OF ORGANIC MATTER TO SOIL OXIDATION.

Oxidation in soils is undoubtedly due to various factors and is dependent not only on the inorganic constituents of the soil, but also on the organic matter. In the case of the Hagerstown loam, the manured soil had by far the best oxidizing power. With the unfertilized soil as 100, the plot which had received ten tons of stable manure to the acre was 136 and over. Decomposing cowpea vines added to sassafras silt loam increased the oxidizing power. When various soils were steam-heated or heated at 105° C. for an hour, the oxidative power was greatly lessened. This decrease in the oxidizing power we have found to be due mainly to changes in the organic matter. When the organic matter of the soil was destroyed by incineration, the oxidizing power was lost. The oxidative power of the soil is dependent on the nature of the organic matter. Thus, when salts of manganese, iron, calcium, magnesium, and aluminum were added to soil of slight oxidative power, oxidation was but slightly increased until certain kinds of organic matter were added, such as citric, malic, tartaric, glycolic acids, or their salts. These compounds we found had a reducing action, converting ferric compounds to ferrous compounds, and probably bring about the stimulation of the oxidative power of the bases mentioned by means of a preliminary reduction to lower, less oxygenated compounds, which, in turn reoxidizing themselves, activate the oxygen of the air. This active oxygen oxidizes other bodies such as organic material of the soil or aloin which is employed as a test of oxidation. It may be, too, that hydroxyacids affect the oxidative powers of complex organic substances or of inorganic-organic complexes.

Fresh plant juices have the power to oxidize aloin directly. On standing, this direct oxidizing power is often lost, either because of change in the reaction of the juices or because the oxidizing principles have undergone changes. After the loss of the direct oxidizing power, the plant juices as a rule have an indirect oxidizing power, that is, they can oxidize with the addition of hydrogen peroxide.

The addition of hydrogen peroxide increased the oxidizing action of some soils, decreased it in others. The peroxide increased the oxidative power of Takoma lawn soil and Cecil fine sandy loam which give no direct oxidation of aloin and decreased oxidation in Sassafras silt loam and Hagerstown loam, manured, which normally oxidize aloin directly. It is possible that the soils which normally give a direct oxidation of aloin contain both organic and inorganic peroxides. It is highly probable that soils rich in organic matter would contain organic peroxides, since such soils have been found by us to have the ability to absorb oxygen. Decomposing cowpea was found to have a strong oxidizing power on aloin, an oxidizing power which was not entirely destroyed in ten minutes'

heating on a steam bath or by carbon bisulphide. That organic bodies will form peroxides in the presence of air is shown by Baeyer and Villiger,¹ who showed that when benzaldehyde is oxidized by atmospheric oxygen, benzoyl peroxide is formed,



and by Ditz,² who found that ethyl ether in contact with air forms within itself more or less ethyl peroxide. This ethyl peroxide he found had a stronger oxidizing action than hydrogen peroxide.

Bach³ concluded that the so-called oxidizing ferments in blood are simply readily oxidizable substances having a special aptitude for forming peroxides which oxidize other substances more difficult to oxidize.

Kastle and Loevenhart,⁴ in discussing the nature of the oxidizing ferment of the potato, concludes that the so-called oxidizing ferment is in all probability not a true ferment, but an organic peroxide. They further conclude that oxidation phenomena occurring in plants and probably also in animals can be satisfactorily explained upon the supposition that the readily autoxidizable substances which they contain are oxidized to the peroxide condition by molecular oxygen and that the peroxides thus formed in turn give up part, if not all, of their oxygen to other less oxidizable substances present in the cell. In other words, the process of rendering oxygen active by the living cell is probably brought about in essentially the same way that this is accomplished by phosphorus, benzaldehyde, and other oxygen carriers, that is, it is one phase of autoxidation.

Peroxide-forming bodies, such as benzaldehyde and peroxides like quinone, have a strong oxidizing action on aloin, both in solution and in soil.

It is possible that, in the soil, complex autoxidizable substances are formed in the changes brought about by the action of microorganisms on plant debris, etc. These autoxidizable substances would combine with the oxygen of the air in much the same way that benzaldehyde does and would form complex, more or less unstable, peroxides which in turn would give up a part or all of their oxygen to oxidizable substances in contact with them or could further oxidize themselves.

The possibility of the formation of peroxides in soil even to excess is indicated by Sjollem and Hudig,⁵ who found that oat-sick soils were restored to a good condition by manganese sulphate and suggested that oat-sickness may be due to the formation in the soil in the presence of excess of calcareous fertilizers and physiological alkaline fertilizers as nitrite of soda, of large amounts of peroxides injurious to plants. The favorable action of the manganese sulphate is due according to these investigators to the catalytic decomposition of such injurious peroxides.

THE EFFECT OF EXCESSIVE OXIDATION.

Whatever induces excessive oxidation in soil or

plant would undoubtedly be injurious. Thus Woods¹ found that excess of the oxidizing enzymes in plants destroyed the chlorophyll. Loew and Sawa² and Salomone³ found that an excess of manganese sulphate added to soil decreased the growth of plants with a great increase of the oxidative power of the plant juices and according to Kastle and Elvove⁴ strong oxidizing agents like nitrates, nitrobenzene, picric acid, chromates, chlorates, arsenates, organic peroxides and peracids are poisonous to life. In small amounts these substances may be stimulative to life functions. In a similar manner quinone, a strong oxidizer, is poisonous to plants such as wheat. Under normal conditions, as in the plant, the excessive formation of peroxide is prevented in some way, either by the further oxidation of the peroxides or by the catalytic or peroxide-splitting power of the soils. Most soils have this catalytic power to a greater or less degree and in general we have found that fertile soils have a greater catalytic power, as well as a greater oxidative power, than infertile soils. The relation between oxidation and catalysis is not as clear as it might be, even in the plant where it has been extensively studied.

According to Chodat,⁵ the only property of the catalase of which we have certain knowledge is its power to decompose hydrogen peroxide to water and molecular oxygen. According to Loew,⁶ Herlitzka,⁷ Battelli and Stearn,⁸ and Shaffer,⁹ on the other hand, the catalase of plants has a protective influence against excessive oxidation. The catalytic power of the soil may in time be shown to have a similar action in promoting normal oxidation in soils and like oxidation may be connected with soil conditions adapted to the growth of the majority of plants.

In the study of oxidation in soils, we have found that most soils will directly oxidize substances in the manner of an oxidase, while a few will oxidize only in the presence of hydrogen peroxide, like the peroxidase reaction in plants and animals. The addition of certain organic hydroxy acids increases oxidation in soils in a way analogous to the activating action of alfalfa laccase and salts of hydroxyacids as discovered by Euler and Bolin.¹⁰ Dilute mineral acids and alkalies check oxidation in soils as they do the oxidation by plant roots or plant juices. The addition of various salts to soils increases the oxidizing power of soil just as Bach¹¹ found mineral salts further oxidation changes of tyrosine by tyrosinase. Again, most soils have more or less catalytic power. In short, it would be found undoubtedly that all the

¹ Loc. cit.

² Bull. Coll. Ag., Tokyo, **5**, 161 (1902-3).

³ Le Staz. Sper. Agr. Ital., **38**, 1015 (1905); **40**, 97 (1907). In connection with the excess of manganese in soil and soil oxidation see also Kelley, Hawaii Sta. Press, Bull. **23**; THIS JOURNAL, **1**, 533 (1909); Guthrie and Cohen, Agr. Gazette of New South Wales, **21**, 219 (1910).

⁴ Am. Chem. Jour., **31**, 195 (1904).

⁵ Schweiz Wochenschr. Chem. u. Pharm., **43**, 626, 642, 655 (1905).

⁶ Report **68**, U. S. Dept. Agr. (1901).

⁷ Rend. Sci. Fis. Mat. et Nat. Real. Acad. Lincei, **16**, Series 5, Part 2, 473 (1907).

⁸ Compt. rend., **141**, 1044 (1905).

⁹ Am. Jour. Physiol., **14**, 299 (1905).

¹⁰ Z. physiol. Chem., **57**, 80 (1908); Z. phys. Chem., **69**, 187 (1909).

¹¹ Ber. chem. Ges., **43**, 364 (1910).

¹ B. deutsch. chem. Ges., **33**, 1569 (1900).

² Chem.-Ztg., **29**, 705 (1905).

³ Compt. rend., **124**, 951 (1897).

⁴ Am. Chem. Jour., **26**, 539 (1901).

⁵ Expt. Sta. Record, **21**, 115 (1909).

various kinds of oxidation going on in plants and animals could be duplicated by a detailed study of oxidation in soil. The oxidation in soil *per se* is due mainly to non-enzymotic forces, inorganic and organic, working separately, conjointly, or in reinforcing or activating combination. In soil oxidation the nature of the organic matters seems to be of great importance. Conjointly with the oxidation in soils which is active whether the soil is planted or unplanted is the oxidizing power of the roots.

CONCLUSIONS.

1. Soils have the power to oxidize aloin.
2. This oxidizing power is increased by adding water to optimum moisture, by the commonly used fertilizers in conjunction with plant growth, by salts of manganese, iron, aluminum, calcium, and magnesium, in the presence of simple organic hydroxy-acids.
3. Oxidation in soil is comparable to oxidation in plants and animals.
4. The oxidative power of the soil appear to be mainly non-enzymotic, the results of interaction between inorganic constituents and certain types of organic matter. It may be brought about by organic matter in a state of autoxidation and by inorganic oxygen carriers such as manganese and iron.
5. Oxidation is greater in the soil than in the sub-soil.
6. Oxidation is greater in fertile soils than in infertile soils.

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THE USE OF NITRATE OF SODA IN COMMERCIAL FERTILIZERS.

By CHARLES S. CATHCART.
Received November 1, 1910.

The value of a commercial fertilizer is measured by its content and form of nitrogen, phosphoric acid and potash. In order to determine this value with any degree of accuracy, it is the practice of the chemists connected with the fertilizer inspections of the several States to ascertain the amount of nitrogen contained in the sample in the form of nitrate, ammonia salts and organic matter. Determinations are made of the total and insoluble phosphoric acid; the difference between the figures thus obtained is the available phosphoric acid, and, in addition to determining the percentage of water soluble potash it is ascertained whether it is to be considered as in the form of muriate or sulphate. From this procedure it is quite evident that sufficient attention is being given to the form or availability of the valuable constituents of this class of materials with the exception of the organic nitrogen. That there is a very great difference in the character, and, consequently, in the availability of the various organic nitrogenous materials used in compounding the mixtures is conceded by all interested, but it seems that the chemists, and others, have been contented to ignore to a certain extent this important question.

Studies on the availability of various nitrogen compounds have been conducted by investigators in Europe and in this country, and the results show that when the recovery of nitrogen from nitrate of soda, which has the highest percentage of recovery, is considered as 100, the relative availability of nitrogen as ammonia is about 70, and from dried blood about 64.5.

At the present time a pound of nitrogen in the form of the water-soluble compounds, nitrate of soda and ammonia salts, can be purchased for four-fifths of the cost of the same amount of nitrogen when obtained from high-grade organic materials, such as dried blood. On account of this difference in the cost and the higher availability of the water-soluble compounds, it is to be supposed that it would be to the best interests of the manufacturers to use these compounds, and more particularly the nitrate of soda, in a large percentage of their brands, since the cost of materials would be diminished and the resultant mixtures would produce more immediate, if not greater, returns. It is needless to state, however, that we are assuming the manufacturers use only high-grade materials. An examination of the following tabulation which was prepared from the records of the inspection for 1909 in New Jersey will show that the supposition regarding the use of nitrate of soda is not strictly correct.

Total number of brands examined.....	483.0
Total number of brands containing nitrates.....	206.0
Per cent. of brands containing nitrates.....	42.6
Total number of manufacturers.....	108.0
Total number of manufacturers using nitrates.....	55.0
Per cent. of manufacturers using nitrates.....	50.9

If the records of this inspection are more closely studied it will be found that twenty or more manufacturers may be considered as having a local business and that they have nearly sixty brands included in the above, and of this number at least fifty contain nitrate nitrogen. If these figures were eliminated from the tabulation, the results would, probably, more nearly represent the facts when considered on the basis of tonnage sold, and the percentage of brands containing nitrates as well as the percentage of manufacturers using this material would be considerably reduced.

Since these facts are somewhat at variance with our supposition, some inquiries were made in order to account for the condition and the principal reasons given were:

I. There is a loss of nitrogen in mixtures containing nitrate of soda.

II. Nitrate of soda causes the fertilizer to become pasty and thus cause trouble when used in the drill.

In order to get some information regarding these two questions, two experiments were outlined; (1) to determine the actual loss of nitrogen, and (2) the mechanical condition.

Experiment I. Loss of Nitrogen.—It is generally admitted that there is a loss of nitrogen in mixtures containing nitrate of soda and acidulated goods, and that the amount of this loss depends largely upon the materials used. In order to determine the actual

loss of nitrogen in this class of mixtures and, also, to ascertain whether the loss is immediate or gradual, a series of mixtures was prepared using a constant quantity of acid phosphate with different amounts of nitrate of soda and muriate of potash, high-grade tankage being used as a diluent. These ingredients were purchased from a large fertilizer company and should be fairly representative.

The plan of the experiment was to make all of the conditions as nearly the same as found in the regular manufacture as possible. With this in view a five-pound sample of each of the formulas was carefully prepared after the composition of the various ingredients had been determined. These mixtures were placed in small bags made of the same kind of material that is used for this purpose by the trade. Two days after the samples had been prepared they were removed from the bags, and, after a thorough mixing, subsamples were taken and examined for their content of moisture and nitrogen. The original samples were replaced in the bags and carefully stored. This operation was repeated at the end of two, four and fifteen weeks.

The results obtained for nitrogen in each of these examinations were computed to the same water basis as that calculated for the original mixture, and the following tabulation will give these results as well as the calculated content of nitrogen, phosphoric acid and potash.

TABULATION.

Sample number.	Calculated composition.					Total nitrogen at end of				
	Phosphoric acid. Per cent.	Potash Per cent.	Nitrogen as			Two days. Per cent.	Two weeks. Per cent.	Four weeks Per cent.	Fifteen weeks. Per cent.	
			Nitrate. Per cent.	Organic Per cent.	Total Per cent.					
A 1	7	4	1.01	3.12	4.13	4.16	4.13	4.09	4.09	
2	7	6	1.01	2.77	3.78	3.76	3.76	3.73	3.74	
3	7	8	1.01	2.43	3.44	3.41	3.43	3.35	3.32	
4	7	10	1.01	2.08	3.09	3.07	3.06	3.05	3.01	
B 1	7	4	1.47	2.86	4.33	4.34	4.36	4.32	4.22	
2	7	6	1.47	2.52	3.99	3.98	4.10	3.96	3.82	
3	7	8	1.47	2.17	3.64	3.65	3.66	3.63	3.44	
4	7	10	1.47	1.82	3.29	3.41	3.34	3.24	3.14	
C 1	7	4	1.94	2.60	4.54	4.48	4.53	4.50	4.29	
2	7	6	1.94	2.25	4.19	4.11	4.21	4.16	4.02	
3	7	8	1.94	1.91	3.85	3.91	3.77	3.81	3.75	
4	7	10	1.94	1.56	3.50	3.46	3.61	3.43	3.34	
D 1	7	4	2.40	2.34	4.74	4.34	4.80	4.70	4.42	
2	7	6	2.40	1.99	4.39	4.46	4.38	4.49	4.29	
3	7	8	2.40	1.65	4.05	4.13	4.05	4.04	3.83	
4	7	10	2.40	1.30	3.70	3.63	3.76	3.61	3.47	
E 1	7	4	2.87	2.08	4.95	4.95	4.85	4.84	4.52	
2	7	6	2.87	1.73	4.60	4.57	4.57	4.47	4.24	
3	7	8	2.87	1.39	4.26	4.11	4.19	4.31	3.97	
4	7	10	2.87	1.04	3.91	3.90	3.81	3.74	3.61	

Inasmuch as each set of samples contained the same quantity of nitrate of soda, the several sets in the series have been averaged as follows:

Set.	Calculated nitrogen.	Found.			
	Per cent.	Run No. 1.	Run No. 2.	Run No. 3.	Run No. 4.
A	3.61	3.60	3.60	3.56	3.54
B	3.81	3.85	3.87	3.79	3.66
C	4.02	3.99	4.03	3.98	3.85
D	4.22	4.24	4.25	4.21	4.00
E	4.43	4.38	4.36	4.34	4.09

By referring to the tabulation it will be noticed that the loss of nitrogen in the first three examinations was not very great and in no case was it a serious consideration, but the results obtained with set E were suspicious. During the entire time of these three periods the atmosphere was very dry and the samples remained in the same condition, practically, as they were mixed, but between the third and fourth examinations, the weather conditions were reversed and the samples absorbed considerable moisture. The content of moisture in the samples as drawn from the bags was not determined, but these figures were obtained for the samples after they had been prepared for analysis. These results, of course, did not give the true content of moisture in the original samples but they indicated the increase. From these determinations it would seem as if the moisture content at the time of the third examination had increased from one to two and one-half per cent. while the last examination would increase these figures to three and one-half to fourteen per cent. As previously stated, all of the nitrogen determinations were calculated to the original water-basis before tabulating and, consequently, the lower results obtained in the fourth examination can not be attributed to the presence of the higher percentages of moisture, but the loss was undoubtedly due to the conditions after the water had been taken up.

It would be unwise to draw a conclusion from a single experiment, but the results indicate that the actual loss of nitrogen would not be of great importance if the materials could be kept dry but that an appreciable loss will occur when there is an absorption of moisture.

Experiment II. Mechanical Condition.—One of the important problems in the manufacture of fertilizers is to prepare mixtures that will remain in a good mechanical condition. It is generally assumed that the presence of nitrate of soda in a mixture will cause the material to become more or less moist, depending upon the amount of soda present, and thus make the fertilizer in a poor condition to be used in drills.

In order to get some data on this question, two series of mixtures were prepared, one of which was the same as used in the previous experiment with the addition of one set of samples which contained no nitrate of soda. The second series was the same as the first with the exception that sulphate of potash was used instead of the muriate. These mixtures were prepared at the same time as those in loss of nitrogen experiment and were, of course, subjected to the same weather conditions. These samples were stored on shelves in a large room and allowed to stand for three and one-half months when they were removed from the bags and subsampled. The moisture content was then determined in each sample. The results obtained may not indicate the maximum quantity of water absorbed, nor the effect that would be produced by having a number of bags stored in a pile, but they are comparable because they were subjected to the same conditions.

The following tabulation will give the calculated

content of moisture in the various mixtures and the amounts found to be present at the time of examination.

TABULATION.

Sample number.	Calculated.			Found. Moisture 3½ months after mixing. Per cent.	Moisture. Differ- ence. Per cent.
	Nitrogen from nitrates. Per cent.	Potash from muriate. Per cent.	Moisture. Per cent.		
F 1	4	10.57	9.30	- 1.27
2	6	10.22	10.10	- 0.12
3	8	9.87	10.40	+ 0.53
4	10	9.51	13.60	+ 4.09
G 1	1.01	4	10.08	14.48	+ 4.40
2	1.01	6	9.75	14.90	+ 5.15
3	1.01	8	9.42	14.90	+ 5.48
4	1.01	10	9.09	15.80	+ 6.71
H 1	1.47	4	9.88	15.30	+ 5.42
2	1.47	6	9.54	16.90	+ 7.36
3	1.47	8	9.22	17.00	+ 7.78
4	1.47	10	8.89	17.95	+ 9.06
I 1	1.94	4	9.67	18.20	+ 8.53
2	1.94	6	9.34	18.05	+ 8.71
3	1.94	8	9.01	18.45	+ 9.44
4	1.94	10	8.68	18.25	+ 9.57
J 1	2.40	4	9.46	18.25	+ 8.79
2	2.40	6	9.14	17.80	+ 8.66
3	2.40	8	8.80	17.65	+ 8.85
4	2.40	10	8.48	18.45	+ 9.97
K 1	2.87	4	9.26	17.95	+ 8.69
2	2.87	6	8.93	17.65	+ 8.72
3	2.87	8	8.60	17.75	+ 9.15
4	2.87	10	8.27	18.15	+ 9.88

TABULATION.

Sample number.	Calculated.			Found. Moisture 3½ months after mixing. Per cent.	Moisture. Differ- ence. Per cent.
	Nitrogen from nitrates. Per cent.	Potash from sulphate. Per cent.	Moisture. Per cent.		
L 1	4	10.65	6.48	- 4.17
2	6	10.34	6.70	- 3.64
3	8	10.03	6.65	- 3.38
4	10	9.71	6.90	- 2.81
M 1	1.01	4	10.16	9.35	- 0.81
2	1.01	6	9.87	9.40	- 0.47
3	1.01	8	9.58	8.60	- 0.98
4	1.01	10	9.29	8.33	- 0.96
N 1	1.47	4	9.96	10.83	+ 0.87
2	1.47	6	9.66	10.35	+ 0.69
3	1.47	8	9.38	10.30	+ 0.92
4	1.47	10	9.09	10.20	+ 1.11
O 1	1.94	4	9.75	11.75	+ 2.00
2	1.94	6	9.46	11.25	+ 1.79
3	1.94	8	9.17	10.72	+ 1.55
4	1.94	10	8.88	10.65	+ 1.77
P 1	2.40	4	9.54	12.38	+ 2.84
2	2.40	6	9.26	11.53	+ 2.27
3	2.40	8	8.96	11.33	+ 2.37
4	2.40	10	8.68	11.35	+ 2.67
Q 1	2.87	4	9.34	14.55	+ 5.21
2	2.87	6	9.05	13.98	+ 4.93
3	2.87	8	8.76	13.27	+ 4.51
4	2.87	10	8.47	13.08	+ 4.61

By a survey of the preceding table it will be noticed that the mixtures prepared with sulphate of potash and no nitrate of soda at the time of the examination contained practically the same amount of moisture and the amount found was considerably lower than the calculated content. The corresponding set prepared with muriate of potash contained different percentages of moisture and the figures increased with the per cent. of potash, but in no instance was the water content as low as in the sulphate set.

The results of these two sets of mixtures would indicate that the sulphate of potash did not absorb much, if any, moisture while the muriate did absorb moisture and the quantity of this absorption was greater as the per cent. of potash increased.

The moisture content in each set of the two series increased with the amount of soda added but in every case the set prepared with the muriate contained more than the corresponding set prepared with the sulphate, and, as found with the set containing no nitrate, the quantity was increased with the per cent. of potash.

All of the samples in the sulphate series, with the exception of set Q, were in a good mechanical condition and those in the muriate set containing 1.47 per cent. nitrate nitrogen and from 6 to 10 per cent. potash were no better than those in the other series which contained 2.87 per cent. nitrate nitrogen. Judging from these results, it appears that fertilizer mixtures can be prepared so that they contain as much as 2.50 per cent. nitrate nitrogen and 10 per cent. potash, stored under severe weather conditions, and will remain in a good mechanical condition, provided the potash is derived from sulphate and not from muriate.

According to the reports of the New Jersey inspections about 6 to 8 per cent. of the brands of commercial fertilizers on the market contain potash in the form of sulphate and, consequently, the poor mechanical condition of many of the commercial brands, after they have been stored for a little time, and particularly those containing a high percentage of potash derived from muriate, can be attributed in part to the muriate of potash that has been used in preparing the mixtures.

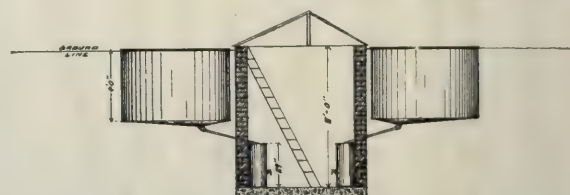
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TANKS FOR SOIL INVESTIGATION AT THE FLORIDA AGRICULTURAL EXPERIMENT STATION.

By A. W. BLAIR AND S. E. COLLISON.

Received August 15, 1910.

While much light can still be thrown on soil and fertilizer problems by carefully conducted field experiments, there yet remain some problems that can never be solved until we can control and measure the factors more accurately than we can in field



TANKS FOR
SOIL INVESTIGATION
FLORIDA EXPERIMENT STATION
Scale 1/4" = 1'-0"

Fig. 1.

work. To supplement the field work in orange culture that the Florida Experiment Station is conducting, and to make it possible to estimate accurately the loss of soluble fertilizing materials in the drainage

waters under different systems of fertilizing, and also to investigate the effects of the long-continued use of commercial fertilizers on the soil and on the orange tree, a series of soil tanks has been set up. Each of these tanks has an inside diameter of 5 feet $3\frac{1}{4}$ inches, with a maximum depth of $4\frac{1}{2}$ feet, and a surface area of one two-thousandth of an acre. The tanks are constructed of heavy galvanized iron (No. 12 gauge), soldered and riveted, and before being placed in the ground they were thoroughly painted inside and out. As may be seen from the accompanying diagrams the bottom of a tank slopes to a point near one side, where there is a strainer opening into a two-inch tin-lined drainage pipe, the length of which is a little more than 4 feet. Four such tanks open into a central collecting pit (one drainage pipe entering at each corner as shown in Fig. 2) where are placed the four receptacles for collecting the drainage waters. Connected with each of these receiving tanks is an overflow tank which is ready for use in case of an emergency (long-continued heavy rains). The collecting pit, which is about 8 ft. deep and 6 feet square inside, is built of brick, with a concrete bottom, and is covered.

The soil tanks were sunk in the ground to within a few inches of the top, and filled with soil to within three inches of the edge.

Over the sloping part of the bottom was placed a layer of smooth quartz pebbles, the coarsest material being placed around the drainage opening and the finest on the top. Above this pebble layer was placed

filling the tanks, the last foot taken from the ground was placed on the gravel in the bottom of the tank, then the next foot, and so on to the top 9 inches. The soil was well tamped as it was put in, each tank



Fig. 3. One of the tanks.

having the same weight of dry soil, 8,625 pounds. The soil is a rather coarse sand, described by the Bureau of Soils as Norfolk sand.

One orange tree has been planted in each tank, and the four trees will be fertilized differently. The tanks are so placed that the trees are about 14 feet apart. Four control trees have been planted a short distance away from the tanks. The tanks are open at the top, and will as far as possible (that is, with due regard to protection from frost) be exposed to natural conditions. Should it become necessary to water artificially, this will be done and a record kept of the amount of water so used. Temperature and rainfall records will also be registered. On the approach of cold waves, the trees will be protected with tents and heaters. It is believed that the tanks will last for a period of 15 years or more, a period long enough for much valuable information to be accumulated. The first samples of the drainage waters have been collected and are being analyzed. Additional series of tanks will be added as means are available.

GAINESVILLE, FLA.,
Aug. 9, 1910.

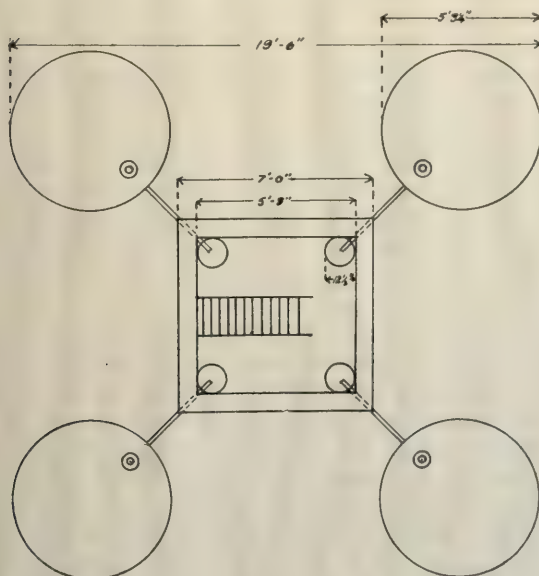
ADDRESSES.

PORTLAND CEMENT AS A BY-PRODUCT.¹

By J. H. KEMPSTER.

In a paper read before the Section about a year ago by Mr. Touzalin, of the Illinois Steel Co., it was stated that while iron is the chief product of the blast furnace, immense industries have been built up from the by-products which for many years were allowed

¹ An address delivered before the Chicago Section of the American Chemical Society, November 25, 1910.



TANKS FOR
SOIL INVESTIGATION
FLORIDA EXPERIMENT STATION
Scale $\frac{1}{4}$ " = 1'-0"

Fig. 2.

45 inches of soil, which was put in the tanks in the following manner. When the soil was dug from the site which each tank was to occupy, the top 9 inches were taken off first, followed by three one-foot sections. All four lots of soil were kept separate. In

to go to waste. Gases are now transformed into power; flue dust is clinkered and recharged into the furnace and slag is granulated and made into Portland cement. Any discussion of Portland cement will be incomplete unless we understand at the outset what Portland cement is and why it was so named.

The cement industry proper dates from the researches of an English engineer, John Smeaton, who had been employed by Parliament to build a lighthouse on a group of rocks in the English Channel. In attacking this problem one of the chief difficulties he had to overcome was the failure of ordinary lime to harden under water. In a series of experiments he found that the pure white limestone ordinarily considered best for lime-making were really inferior to the soft clayey ones, for from the latter he produced a lime that would harden under water. Such a stone was found on the coast of Cornwall, and the hydraulic lime formed by burning this stone was the basis of the mortar used in the construction of the Eddystone lighthouse.

In 1824 Joseph Aspin, a bricklayer of Leeds, England, took out a patent on an improved cement which he proposed to make from the dust of road repaired with limestone or else with limestone itself combined with clay, by burning and grinding. This cement he called Portland cement because when hardened it produced a yellowish gray mass resembling in appearance the stone from the famous quarries at Portland, England (these discoveries are now incorporated in our definition of Portland cement).

According to the standard specifications, "Portland cement is the finely pulverized product obtained by grinding the clinker resulting from the calcination to incipient fusion of an intimate mixture of properly proportioned argillaceous and calcareous materials, to which no addition greater than 3 per cent. has been made, subsequent to calcination." Cement may be looked upon, for sake of illustration, as the reaction product between an acid and a base, the lime taking the basic, and the silica and alumina the acid side of the equation. A part of the alumina is replaced by iron oxide and a part of the lime by magnesia. Thus we can readily see that the manufacture of Portland cement is not limited to one particular form of rock, but may be made from any material furnishing the desired elements.

Slag furnishes the silica, alumina and a part of the lime. Slag to be suitable for making cement should contain about $2\frac{1}{2}$ times as much silica as alumina, and have a low magnesia content. Magnesia in cement causes slow cracking and disintegration if present in sufficient amount, therefore many specifications call for not over 4 per cent. in the finished cement; some call for less than 3 per cent. In order to produce such a slag the furnace is charged with a low-magnesia limestone.

While we are speaking of Portland cement made from slag and stone it might be well to make a distinction between this product and so-called slag cement. Slag cement is a term applied to cement made by intimately mixing, by grinding together,

granulated slag and slaked lime without calcination subsequent to mixing. I wish to make this distinction clear. If you grind lime with slag your product is a slag cement, but if you take the same slag and add to it the proper amount of limestone, burn it, and grind the resulting clinker, you have fulfilled all requirements of a true Portland cement.

A cement plant constitutes a laboratory on a commercial scale. We grind some limestone and we grind some slag. We mix these according to formula and grind them again. We put this mixture in a crucible and heat it to incipient fusion. Cool this clinker and grind to an impalpable powder (adding 2 per cent. of gypsum to control the set) and we have cement.

Briefly, the mechanical processes through which the material passes are as follows: The stone first passes through a gyratory crusher which reduces it to $1\frac{1}{2}$ in. down and discharges into a bucket elevator. The elevator raises the material to the feed spout of the rotary drier. The rotation of the drier gradually works the stone toward a flame. Similar driers are used for slag, no crushing being necessary. The preliminary grinding of both slag and stone is done in ball mills. This is done by the pounding of steel balls on steel grillage plates inside a revolving shell. From the ball mills the material is conveyed to twin hoppers from which the slag and stone are delivered into opposite hoppers of the automatic weighing device. These scales deliver at each dump a certain amount of slag and stone, depending on their analysis. More will be said about this later. After mixing, the material is further ground and mixed in tube mills.

The tube mill consists of a steel drum with cast iron ends about 22 feet long and 5 feet in diameter. Inside is a white iron lining cast in sections and bolted to the shell. The mill is partially filled with flint pebbles, and by their pounding on each other while the mill is revolving, the raw mixture already finely ground is pulverized still finer. It is now ready for burning. The essential features so far are that the material must be properly proportioned, intimately mixed and very finely ground.

The kilns in which the burning takes place vary from 60 to 150 feet long and 6 to 8 feet in diameter. It consists of a brick-lined steel shell supported at two or more points on heavy rolls. Each kiln is set on an incline with the higher end enclosed in a housing from which the waste gases escape into the stack. At the lower end is a movable brick housing through which the air and coal pipe projects. In operation the kiln is rotated at a speed of about one revolution per minute. The raw material is fed into the kiln from a feed pipe and slowly works its way to the discharge end, during which time the clinkering takes place. To protect the steel shell from the intense heat a fire-brick lining is used. The bricks are 9 inches thick at the firing end and 4 inches at the stack end. Powdered coal blown in with a blast of air is used for burning the clinker. Powdered coal blown through a round pipe forms an axial flame, the hottest part of which is in the center of the kiln. The heat, there-

fore, that does the clinkering is the radiant heat from the axial flame. Attempts to use the more effective impinging flame directly on the material have been abandoned because of too rapid burning of the fire-brick lining.

The reactions taking place in the charge in the kiln are the driving off of the carbon dioxide and the sintering of the rest of the ingredients to form the clinker. This sintering of the residue after the carbon dioxide has been burned off is really the chemical union of lime, silica and alumina, etc., giving out heat in the reaction. By burning a given weight of mix with a coal of known heat value this heat of formation of clinker has been determined. By calculating the heat of decomposition of calcium carbonate and subtracting heat of formation of clinker we find that less than twenty pounds of coal are required theoretically, to burn a barrel of clinker. Since the dissociation of calcium carbonate takes place rapidly at 700° to 800° C., and clinkering at 1200° to 1300° C., heat losses, bound to occur while maintaining these high temperatures, bring the amount of fuel required up to many times this amount.

In order to get good combustion an excess of air is blown in with the coal. This excess of air, together with the combustion gases, is introduced into the stack at a temperature ranging from 600° C. to 700° C. This stack is about four feet in diameter, and the velocity up the stack is something like 1800 feet per minute. Without any scientific data, it is evident that the heat loss here is enormous. The tendency in the newer mills is to cut down this loss by the use of longer kilns. I believe there is one operating on the Hudson 232 feet long.

There is need also of a suitable insulating material to back up the fire-brick lining of the kiln in order to cut down the heat loss by conduction. Asbestos has been tried, but was found to be too yielding in character.

The clinker leaves the kiln at about 1050° C. This loss, like others mentioned, has not been as closely watched as one might expect considering the present financial state of the cement industry. Abroad this clinker is run through an undercooler, thereby giving up one-half its heat to the air entering the kiln.

Properly burned Portland cement clinker is greenish black in color and usually when just cooled it is covered with glistening specks. It forms in lumps from the size of a walnut down. The operation of burning requires a workman of experience and good judgment to tell when the kilns are hot enough to burn the material properly. He has the coal feed and air adjustment under his control.

The coal used is a good grade of bituminous coal having a low moisture content.

After the clinker has cooled a clam-shell bucket lifts it into hoppers over the finishing mill crusher. In the process of grinding two sets of machinery are used, the preliminary grinders and the finishing mills. Kent mills crack the clinkers down to the size of wheat and finer. After passing this process the clinker goes through an automatic weighing device which

adds 2 per cent. of plaster of Paris (or gypsum). This mixture is now ground to powder in tube mills when it is ready for the stock-house.

The same mill could, with very little change, be used to make cement from any other raw material.

These mechanical details show the care that is taken that a uniform chemical composition may be obtained. In order to get the best product and a mixture that will burn well, the ratio of the lime to the silica and alumina must be controlled within narrow limits. There must be enough lime present to combine chemically with the acids present and leave no appreciable excess. Uncombined lime combines with water to form calcium hydrate and with carbon dioxide to form calcium carbonate. These reactions, in set cement, cause expansion or blowing and unless such cement is allowed to cure in the air before use, it will not stand the boiling test. On the other hand, if not enough lime is present to take care of the silica and alumina the excess is like too much clay and the tensile strength will be lower than normal.

The chemist has charge of the mixing of these materials, which is simplified by the large units of manufacture. The materials are handled in such large quantities and pass through so many stages of preparation that variations in the mixture are to a great extent eliminated. As a check both on the mixture and the raw material scales, frequent samples are taken and analyzed. The slag is inspected before it leaves the furnaces and only those slags are accepted that have the proper chemical composition. We can therefore calculate our mixture on the lime basis. Silica and alumina are already in the right proportion and it is only necessary to add enough limestone to bring the lime to the required percentage. A formula frequently used in calculating cement mixtures is: $\text{CaO} = 2.8 \times \text{SiO}_2 + 1.1 \times \text{Al}_2\text{O}_3$. Having the analysis of stone and the slag, the ratio may readily be calculated as follows:

ANALYSIS.		
	Limestone. Per cent.	Slag. Per cent.
SiO ₂	1.80	35.40
Al ₂ O ₃	1.30	14.60
CaO.....	52.90	46.30
CALCULATION.		
		Limestone.
SiO ₂	$1.80 \times 2.8 =$	5.04
Al ₂ O ₃	$1.30 \times 1.1 =$	1.43
		6.47
		Slag.
SiO ₂	$35.40 \times 2.8 =$	99.12
Al ₂ O ₃	$14.60 \times 1.1 =$	16.06
		115.18
CaO = 52.90		115.18
—6.47		—CaO in slag 46.30
46.43		68.88
Then: $\frac{46.43 \times 1000}{68.88} = 674.$		

Therefore 1000 parts stone require 674 parts slag by weight. This formula is based on the supposed existence of the tricalcium silicate. The best author-

ities on the constitution of Portland cement are agreed that calcareous hydraulic cements do not represent well-defined compounds, but mixtures of calcium silicates and calcium aluminates with varying amounts of uncombined calcium oxide. The prevailing opinion since the time of Le Chatelier that a tri-calcium silicate existed in Portland cement is now definitely discarded by men of science. However, the formula has served as a practical working basis for the manufacture of cement.

As a further check on the composition, frequent tests are made on samples of clinker taken from the kilns.

The percentage of sulphate in the cement is also closely watched. I have already said that an automatic weighing device mixes the gypsum with the clinker in the process of grinding. As mechanical devices are apt to get out of order in this process also, eternal vigilance in the way of frequent tests is the price of a uniform product.

CHEMICAL LABORATORY,
UNIVERSAL PORTLAND CEMENT CO.,
BUFFINGTON, IND.

THE TRAINING OF CHEMICAL ENGINEERS.¹

By M. C. WHITAKER.

Much attention is properly being centered upon the education of men in the scientific development and management of agricultural production, and the Government not only gives direct financial support to a large number of schools for such training, but also maintains a Department of Agriculture, the function of which is largely educational.

The annual production of the chemical industries is almost equal in value to the agricultural production of the country, and it is therefore proper to compare the facilities now being provided and the means now being adopted for the education of men to develop and manage the widely diversified units of chemical manufacture with the methods and facilities in other educational fields. Obviously the general educational and technical equipment of men to develop and direct processes or works depending upon the applications of chemistry, and usually involving a knowledge of power and mechanical and electrical machinery, is much greater than the technical equipment required for men in agricultural production. While agricultural education has grown and developed at a rate commensurate with the producing power of that industry, and has been fostered by private, State and Federal funds, education in the equally important and essential field of chemical manufacture has been, in some institutions, entirely ignored, in others only indifferently provided, and in no single case supported and equipped on a basis comparable with the wealth-producing power of the industry.

Efficient production and the economic management of our manufacturing plants are essential features to our commercial development, and it is in this field that the greatest results are to be attained in the conservation of our natural resources. The accom-

plishment of these results obviously depends upon the application of scientific knowledge to the solution of all problems, both great and small, in the development, the direction and the management of our factories.

The chemical industries very properly look to the schools for men qualified to produce these results, to improve their production and manage their works. The best evidence that more and better trained men are needed in the chemical industries is the fact that this Institute of Chemical Engineers, composed of men of experience and men now engaged in the direction of great industries, meets twice a year and devotes a large portion of its time to the study of the problem of how to obtain trained men to assist them in the development and administration of their work.

Every employer of chemical talent knows that at best the young graduate is only a vague "prospect" and that much has been left undone in his training.

The problem of proper training and correct methods of teaching chemical engineering is one which must be carefully analyzed and studied from its very foundation and is not one to be remedied by a few trivial changes in existing curricula—by dropping this and substituting that. The subject must be opened up and examined to its foundation and if it is found that the present structure is built on sand we should put some "concrete" under it.

Necessarily, the problem must be solved by the coöperation of the teachers with the employer of chemically trained men, and the writer, having served a term of practically ten years in each of the above fields, begs to submit a few observations and conclusions for the consideration of the Institute Committee.

The chemical industries require for their development and management two classes of men of somewhat different training, natural qualifications and range of service.

FIRST.—*Research Chemists* who are qualified naturally and by training to originate and to develop in new fields. The training of the research man is more advanced, or supplements that of the chemical engineer, and the research results furnish the foundations for the industries which the chemical engineer organizes and administers. In other words, the research chemist works in the new and undeveloped fields of chemical knowledge and produces results calculated to contribute new knowledge and new arts.

SECOND.—*The Chemical Engineer* works in the organization, operation and management of existing or proposed processes with a view to building up a successful manufacturing industry. He uses his classified knowledge of chemistry and the allied engineering branches in developing, perfecting, organizing and administering a plant or a process for the production of a marketable and useful product at a profit to the investor.

Such a field as this requires a man of knowledge, originality and resourcefulness. His fundamental training in chemistry, physics, mathematics, etc., must be thorough and must be combined with a natural

¹ An address presented to the American Institute of Chemical Engineers, December 7, 1910.

engineering inclination and an acquired knowledge of engineering methods and appliances. His originality and imaginative capacity seems to me to be essential and a combination result of natural qualifications and training. Resourcefulness, however, comes as a result of experience in application and the ability to adapt a wide range of methods and practices to new conditions. A man with the natural qualifications, supplemented by the proper training, may become a successful chemical engineer.

The success of the research chemist is measured by his scientific achievements, whereas the success of the chemical engineer is measured by his commercial results. While their work bears a certain mutual and cyclic relation it must be apparent that their natural and educational equipment may be entirely different.

The development of specialized training in certain selected lines of manufacture is not a proper function for an engineering school, but should be left to the trade school or to the industries themselves. Specialized research, on the other hand, should be carefully eliminated from the regular engineering training and provided for in graduate courses.

For convenience in discussion, I have divided training subjects for the chemical engineer into three general classes: Fundamental, Associated and Supplementary. No attempt is made to discuss the details of the curriculum, the general purpose being to get broad subdivisions as a starting point. The question of arrangement of subjects into a curriculum and the proper allotment of time for the course depends upon what is finally determined as proper training for the men under discussion:

Chemistry	}	Fundamental training.
Physics		
Mathematics		
Allied subjects		

Electrical Engineering	}	Associated training.
Mechanical Engineering		
Civil Engineering		
General Engineering		
Business economics		

Study of the applications of the fundamental and associated training in laboratories equipped with the "tools of the trade" and with working plants.	}	Supplementary training.
Training, by "contact" and by "example," in a laboratory managed as an approved business, in the principles and practices of efficient organization and administration.		

FUNDAMENTAL TRAINING.—The training in the fundamental subjects need not be materially changed except perhaps more attention should be given to the laboratory facilities and to the selection of instructors for the fundamental work. Profound scholarship and a record for original research are too often made the sole determining factor in the selection of teachers for these subjects. Research qualifications are of secondary importance in the selection of men to give the fundamental training to our chemical engineers. Such teachers might better be chosen from men physically, temperamentally and educationally qualified to present their subjects clearly, logically and enthusiastically to the student, and to present them

in such a way as to quicken and hold his interest. Too often our undergraduates become muddled, discouraged and even give up a subject because of its dry, disconnected presentation or because the instructor "talks over their heads" or lacks the personality and the power to interest them. Research instructors are often permitted to emphasize their "hobbies" or to teach their special experiences without regard to the purpose of the course and its relation to the fundamental training. Our instructors should always be chosen to fit the course requirements and should not be permitted to divert the work into special fields not contemplated in the basic formulation.

The training in the fundamental branches should be more thorough and carefully proportioned than at present, keeping in mind that the chemical engineer's knowledge must be classified, complete and accurate in the broad principles and not statistical, encyclopedic, or of the class of deep profundity require for research in new, and original fields. The chemical engineer's knowledge is to be used as a basic "tool" of his trade and may be given as such without detracting one iota from its value as mental training.

ASSOCIATED TRAINING.—Associated training is for the purpose of placing in the hands of the chemical engineer a working knowledge of the other engineering branches, so that he may utilize them in the development and management of his particular problem. Courses designed primarily as foundational for future advanced study in the same field are not likely to be proper courses for this associated training. Our associated courses should be broad and general and need not carry the student beyond the foundational principles of the subjects with a working knowledge of the existing design, construction, materials, operation and use of engineering appliances.

The existing methods of teaching by lectures, demonstrations and laboratory work, combined with a liberal use of text and reference books, is probably the most effective way of reaching the fundamental and the associated subjects.

Assuming that the student now has a thorough fundamental foundation in the basic principles of his profession and a working knowledge of the associated engineering branches, schools should be equipped for *directed* study of their *application* to the problems of manufacture and production. This applied study is classed as "supplementary training."

In the education of teachers, in the education of doctors, in the study of agriculture and in the education of all other engineers except chemical engineers, training in the *application* of the respective fundamentals, under the direction and with the assistance of experienced teachers, is considered essential. Medical schools without hospitals, teachers' colleges without practice schools, schools of agriculture without experimental farms, or engineering schools without laboratories and shops would hardly be dignified by classification as schools. Such institutions invariably invest large proportions of their resources in facilities for demonstrating the proper practical application of the fundamental theories.

Is there any reason why chemical engineering should not and could not be taught by the tried methods of the normal schools, the medical school, the agricultural schools and other engineering schools? Only with proper chemical engineering laboratories, equipped with real working models of standard appliances to illustrate the basic applications of the industries, and a proper curriculum arrangement to permit the student to study and use these appliances and the principles involved in their application will we be on a basis comparable with the methods and the facilities now existing in other educational fields.

But we can accomplish still more with proper laboratory facilities. We can so construct and administer these laboratories that the student will be surrounded by an "atmosphere" of manufacturing and business efficiency, where he will learn by *example*, by *daily contact*; by "*attrition*" the modern methods and practices of office and works management. Chemical engineers should have this knowledge. It is fundamental to the proper fulfilment of their job. Instances where failure has been converted into success and industries saved by knowledge of proper administrative practices, and the application of business and works efficiency method, are too numerous to mention. Refinements in chemical processes and ingenious mechanical devices are all ineffective and often useless if inefficient organization and management are permitted to absorb the earnings. Successful chemical manufacturing is based upon three general principles: First, chemical and physical facts; second, mechanical applications; third, organization and management.

The first principle is definite and basic and is, therefore, not capable of variation, but the second and third are variable and may be far from perfection. The greatest opportunity for increased profit therefore lies in the possibility of mechanical improvements and improvements in the efficiency of the organization. Instruction is provided in a greater or less degree in existing schools in the two first principles mentioned, but the third equally important and fundamental principle is not even undertaken.

The "contact" system which I am urging for adoption as a method for teaching the principles and the application of chemistry to manufacture, and for imparting a knowledge of the principles and practices of efficiency in organization, management and administration, is the same as the methods which have always obtained, by force of circumstances, in country schools where the small children in the A, B, C classes unconsciously absorb geography, history, arithmetic, etc., by hearing, seeing and being in the "atmosphere" of the more advanced work. This method can be adopted in the training of chemical engineers and can be made infinitely more effective than in the country school.

The contact or "frictional" method would require a laboratory plant larger and more comprehensive than anything yet established and would have to be managed on somewhat different lines than those now obtaining in engineering schools.

If it is proposed to direct the student in the study of the *application of fundamentals of factories, factory appliances, factory processes and manufacturing business* by the "frictional" method, the laboratory should be equipped, organized and administered as a live manufacturing proposition. There should be ground space enough to permit of the erection of one or more complete operating plants in addition to the general laboratories for the study of great applications such as distillation, evaporation, filtration, wet reactions, high temperature oxidation, electrochemistry, etc.

The complete plants should be chosen from some of the important chemical processes of great common interest, which at the same time illustrate a wide diversity of chemical principles and appliances and products—for example, the manufacture of gas.

These plants should be designed and built from the foundation to the roof so that the structure itself, materials used, equipment and arrangement, would illustrate the best known practice and permit of the most economical management and operation. Every structural detail should be provided with a view to *educating by example*. Office appliances, office systems and facilities should be provided and the equipment includes books, trade journals, patent literature, samples, advertising matter, house organs, etc., of the business. Conference facilities should be provided in each laboratory for lectures, discussions, demonstrations of the chemical, mechanical and business features of the process. All such work should be conducted in the special laboratories, and the student from the time he enters until he leaves should be made to "stumble over" the tools of his art and become "saturated" with the "atmosphere" of the business from the raw material to the market.

The classes should "go the rounds" of the laboratories in convenient sized sections for conferences and for "manning" the work.

In connection with the chemical engineering laboratory there should be a "shop organization" consisting of competent mechanics, helpers, and laborers, necessary for the up-keep of the plant, and this organization should be administered that our students would gain actual experience in dealing with workmen. Office experience, correspondence, dictation, filing and recording, fundamental costing, etc., may all become familiar knowledge to the student by having these facilities arranged for his use and by incorporating them in his daily "business."

TECHNICAL ADVISERS.—These laboratories of engineering chemistry should be organized with a system of technical advisers to be selected from representative experts in each typical field of industrial chemistry. These advisers should be specially qualified experts or active works managers of live concerns. Their connection with the laboratory should not be merely nominal, but should carry with it a responsibility for the proper equipment of the special laboratory of the industry which they represent. They should also give some lectures upon their specialty, not altogether from the chemical standpoint, which presumably can be covered by the regular instructors,

but from the business, organization, and relative industrial standpoint.

The personal contact and acquaintance between adviser and student is an obvious mutual benefit. The attitude of the leading industries towards such a chemical engineering school would become one of personal interest instead of one of criticism.

The technical advisory system, if properly initiated and administered, will insure modern equipment, methods, and instruction in chemical engineering and will give, through the lectures, first-hand and accurate general information on the scope and magnitude of the typical industries. Furthermore, it will definitely dispose of the frequent reference to obsolete and antiquated methods and equipment. By relying upon the judgment of these experts and managers of live and paying industries we would avoid the equally dangerous extreme of becoming loaded up with impractical untried appliances and uncommercial processes.

INDUSTRIAL RESEARCH.—The largest industrial corporations, such as the General Electric Company, the United Gas Improvement Company, the National Electric Lamp Association, etc., have established and are maintaining research laboratories. These laboratories are directed in their chemical and physical research by able and high-priced men and are equipped and maintained at great expense.

Such laboratories are being established because there are no existing equipments, on a suitable scale, for solving the problems necessary for their industrial advancement. The corporations have not undertaken the burden and expense of academic research from choice but from necessity. Our scientific institutions have utterly failed to provide the facilities for industrial research, and as a consequence are being "elbowed" aside from their natural position of technical and scientific leadership.

Under existing conditions the small manufacturer, who can not afford to equip and maintain a research laboratory, has no prospect of solving his industrial problems. Unless the scientific institutions develop modern chemical engineering laboratories, equipped with the tools of the industries, and place their facilities within the range of the small manufacturers, industrial development will be limited to the few concerns whose means will permit the establishment and maintenance of laboratories for private research.

On the other hand, with such laboratories as I have outlined, equipped with every facility for experimentation on a large scale, factory managers, technical laboratories and individuals could be interested in availing themselves of these facilities and in establishing industrial researches for solving industrial problems.

Frequent reference has been made to the cost of such a laboratory of engineering chemistry as has been outlined. We are dealing with a great industry and a great problem and we should therefore exercise our sense of proportion. It is estimated that the minimum *net profit* of chemical manufactures is \$300,000,000 annually. It is also estimated that the

combined investment in chemical engineering equipment in all of the educational institutions of the country is not over \$30,000 or one-hundredth of one per cent. of the net profit of the industry for one year. A thirty thousand dollar investment or even one hundred times that is an absurdly small equipment to be devoted exclusively to instruction in the application of chemistry for such an enormous and profitable industry, not to mention the facilities for research development. If the plan outlined will produce men better qualified to enter this field of industry and men who can "deliver the goods," I have no fear that the question of cost will ever prove an obstacle to the development of such laboratories of chemical engineering.

THE DEVELOPMENT OF PAINT FORMULAE.¹

By L. S. HUGHES.

Until very recent years there was no technology of paints worthy of the name; in fact, it is not too much to say that there was no understanding of the causes of success or failure of any formula. It was recognized in a vague way that a zinc paint was likely to peel and that the addition of non-drying oils led to difficulties; and certain pigments were accepted as valuable, but the art of combining the various available materials was purely empirical; each formula was tried out without co-ordination of its results with the results of other mixes.

The reasons for the long persistence of this condition are not hard to recognize: first, there were no comprehensive or reliable methods for the testing of either pigments or paints. Chemical analyses, even when correct, failed to account for the wide discrepancies observed in the behavior of paints of similar chemical composition, and this method of examination fell into total disrepute among a majority of painters and paint manufacturers. And, second, there was a wide-spread feeling that the value of a paint was in some occult way proportionate to the cost of the raw materials. Indeed, this curiously illogical idea is, even to-day, so widely spread that it is the basis of advertising by many large manufacturers. Third, and last of the important factors in delaying the development, was the very general fraud practiced for the purpose of taking advantage of the belief just mentioned, that is, the manufacture and sale of paints under secret formulae and their sale under guarantee of containing nothing but recognizedly expensive pigments. As some of these mixtures, very largely cheapened in cost by the addition of native mineral pigments, were far superior to their nominal composition it necessarily followed that the latter obtained the credit and so the advantage of "purity;" *i. e.*, freedom from anything except white lead and zinc oxide became a very general criterion of excellence.

So long as this general misrepresentation continued and there was no certain method for testing a paint save by using, it is not unnatural that paint-making failed to become subject to proper technical control.

¹ An address read before the Chicago Section, American Chemical Society, December 16, 1910.

At last, however, some large manufacturers, especially those who manufactured paint for their own use, and some independent chemists began the practice of subjecting all raw materials to regular and thorough examination. At first the data were of little value except in securing uniformity in supply, but as the microscope came more and more into use conjointly with improved chemical methods it became apparent that structure and size of particle were of no less importance than chemical composition; further, the fact began to receive recognition that all of the natural pigments suitable for use alone (or "straight") were heterogenous in size and almost invariably so in structure. This was at first misinterpreted into a rule which, while it contained the elements of an important truth, was nevertheless inexact as stated. The rule at first was that the finer the pigment portion of a paint the better. To prevent possible misunderstanding it is perhaps advisable to anticipate a little and to say here that the more modern form of this dictum is that the finer the major pigments in a paint the better, but that there is advantage in the presence of a moderate portion of distinctly coarser particles.

The apparently mysterious fact that the addition of transparent crystalline ingredients to most of the opaque pigments improved the hiding power of the latter proved a stumbling-block for a long time but was finally elucidated by a demonstration that showed this to occur only when the transparent materials were coarse enough to afford points for capillary action, thus increasing the thickness of the coat. It naturally followed and, indeed, was proven that the diameter of the larger particles was coincident with the thickness of the coat.

These two points were of no little importance because they established a sharp differentiation between "opacity" and "hiding power," two characteristics which had been badly confused and generally regarded as identical.

These investigations were accompanied by coincident interpretation of the chemical behavior of the various ingredients. At first this concerned itself only with the behavior of the straight pigments and the results found expression in many hopeless contradictions. As an instance: because silica, barytes and other crystalline earths of manifest chemical inertness failed entirely when used alone the erroneous idea grew up that unless a pigment were sufficiently basic to react with the oil of the coat it was of doubtful value. As a matter of fact the preponderance of evidence was enormously on the other side from the recognized superiority in wear of the demonstrably stable iron oxides, many dry colors and especially of the totally non-reactive carbon pigments. The difference in color of these from the white pigments was apparently the reason for their lack of consideration—a thing which to-day seems so totally inadequate as to approach the incredible.

Many paint men were never satisfied of the correctness of this belief but it was so generally accepted as to lead to legislative action by one state in the form of a law which directly encouraged paints made only

from basic lead carbonate and zinc oxide, two highly reactive pigments. The phrasing of this act indirectly stigmatized all other ingredients as adulterants.

Even at the time of the passage of this law a consideration of the previously disregarded data of the wear of inert colors and a recognition of the value of the comparatively new basic sulphate white lead had led to a grave suspicion that saponification and analogous reactions were not only of no benefit but were emphatically destructive. This view spread rapidly because the great spread of micrographic study of paints furnished a complete explanation of the failure of the stable crystalline pigments when used alone. Their noticeable coarseness and the universality with which their amorphous analogues proved successful needed little interpretation to show that it was not the chemical stability of the crystalline materials which caused their failure when used alone but that their angular outline and absence of small particles gave a coat possessing interstices of appreciable dimensions, and these being filled with nothing but the easily perishable "linoxin" afforded little resistance to weather attack. Addition of impalpable amorphous substances entirely remedied the weakness of the crystalline pigments except in so far as their undue proportion limited the area covered by the paint.

The work of the late Dr. Dudley and others outlined the general means by which the permeability of a paint coat by moisture and gases may be controlled and the necessity for heterogeneity of structure and composition became very generally recognized.

Satisfactory demonstration of the applicability of these various principles proved of no little difficulty, largely because there was little co-operation between the different experimenters and partly because of what appeared to be hopeless discrepancies between the record of exposure test of analogous formulae in different localities. In a general way it had been acknowledged that a given formula was better adapted to certain classes of work and locality, but there was a strong underlying opinion that a really good paint would be successful under any conditions.

It is easy to be wise after the fact but in the present light of the very comprehensive and valuable records of the co-operative test fences the local success of many paints contrasted with their failure outside of the range of the climatic condition prevailing at the factory where they were tested and developed would seem necessarily to have suggested the necessity or at least the desirability of adjusting formula to climate. It is true that suggestions toward this end have been made but they are merely tentative.

It remained for Mr. John Dewar in his valuable review of test fence records to make the declaration that no one formula can prove satisfactory under all climatic conditions. This dictum is the latest in paint development and with it we may properly close a recital of the gradual development of paint-making rules and turn briefly to a consideration of their application to the use of those pigments which are in general use.

First, a citation of the records of condition of the

white pigments used straight as developed by their exposure at Atlantic City is instructive in illustrating the fallacy of the doctrine of "purity" as a criterion of reliability.

Basic lead carbonate: type A.....	Condition bad.
Basic lead carbonate: type B.....	Condition bad.
Basic lead carbonate: type C.....	Condition bad.
Zinc oxide.....	Condition fair.
Zinc oxide (another test).....	Condition not stated.
Sublimed or basic sulphate white lead	Condition good.
Zinc lead.....	Condition good.

These tests were closely confirmed by the exposures at Pittsburgh although the character of wear in the two sets of tests was naturally quite different.

The remarkable consistency with which the fumiform or sublimate pigments outlasted their pulverized and precipitated competitors is strikingly indicative of the benefit of impalpable fineness and amorphous structure in the major pigment of a mix.

Without exception the individual pigments showed improvement in behavior when employed mixed with others; the prohibitive hardness of the zinc oxide coat was greatly modified by addition of either of the white leads; the checking of the lead carbonates and their tendency towards discoloration were diminished by large admixtures of either zinc oxide or crystalline ingredients, while the sublimed or basic sulphate white lead, which (like all the straight leads) exhibited a soft coat, was satisfactorily hardened when tempered by the addition of zinc oxide.

The recognized difficulty of securing satisfactory brushing with fumiform pigments only, proved easy of elimination by the employment of small amounts of coarser and crystalline pigments. Most satisfactory of all, perhaps, was the demonstration that the characteristics of a pigment persist in mixtures and are manifested proportionately to its amount therein.

A complete demonstration of the advantage of modifying the faults of one pigment by mixing it with others of different qualities is at least strongly indicated by the record of six out of seven successful exposures of paints containing four pigments each.

So consistent was the improvement noted with increasing heterogeneity that the committees in charge of the experiment have made unqualified declaration of the superiority of formulae containing both lead and zinc in addition to mineral crystals.

Attention so far has been given only to the tests at Atlantic City and Pittsburgh because the climatic conditions to which they were exposed are representative of much more important areas than the other series of public tests—those at Fargo, North Dakota.

That the latter have confirmed the generalizations of the Eastern tests is best shown by quotation from a report on the Fargo fences:

"It was conclusively demonstrated that mixtures of white lead and zinc oxide properly blended with moderate percentages of reinforcing pigments, such as asbestine, barytes, silica and calcium carbonate, have proved most satisfactory from every standpoint and are superior to mixtures of prime white pigments not reinforced with inert pigments.

"The white leads painted out on the 1908 fence exhibited different degrees of checking: the mild process lead and sublimed white lead which presented the best surfaces, were free from checking, while the old process leads seemed to be showing very deep and marked checking, even after one year's wear."

While the generalizations were thus borne out by the Dakota tests it must be said that the limits of usefulness of the various "prime" (or opaque) pigments were differently indicated. In the sea coast and Pittsburgh tests very little trouble was noted in securing satisfactory adherence to the painted surface; the difficulty seemed to be to prevent undue permeation of the film by destructive gases and vapors—a problem most satisfactorily solved by the employment of the excessively fine fumiform pigments. As the humidity was always fairly high in these exposures the brittleness, due to hard coats with consequent splitting or peeling, was not noticeable.

In North Dakota, however, the aridity and wide range of temperature almost reversed the problem, and while very few coats perished by disintegration many paints failed through lack of adherence and through undue hardness. The high lead mixes with their consequent softness proved best and the advantage of reducing the zinc oxide content for this region was demonstrated.

A universal improvement in wear was observable in the tinted paints over the untinted made from the same "white base" in all tests without regard to locality—a difference so marked that it is doubtful whether it can be entirely accounted for by consideration only of the increased proportion of chemically stable pigments and the necessary increase in heterogeneity of structure. It appears probable that explanation must await a better understanding of the effect of light within the paint film.

These various tests, confirming, as they do, previous research, bid fair to put paint compounding upon a proper technical basis.

The formulae of to-day can be compounded to secure definite permeability, definite hardness (by proportioning the lead and zinc pigments) and certain attachment to a surface, either by use of a chemically stable fumiform pigment of sufficient fineness to enter the pores of wood or through insuring a soft coat by avoidance of zinc or other hardening agents. Thickness of coat can be accurately controlled by the amount and size of crystalline pigments employed, and checking or internal disintegration can be avoided by the selection of non-reactive and insoluble pigments. Indeed, it is not too much to say that the major functions, at least, of our available pigments have been accurately catalogued.

While much remains to be done (especially in improving the vehicle) the rapid progress that has been made in developing a scientific basis for paint compounding must be regarded not only as satisfactory but as gratifying.

NOTES AND CORRESPONDENCE.

DETERMINATION OF TIN AND ANTIMONY IN SOFT SOLDER.

The following details for the rapid volumetric determination of tin and antimony in soft solder are adapted from A. H. Low's method.¹

Antimony.—On a counterpoised watch glass weight exactly 2 grams of filings, which should be fine enough to pass a 30-mesh sieve. With a quill brush transfer the filings through a stemless funnel into a 300 cc. Jena Erlenmeyer flask. Add 5 grams of KHSO_4 crystals and 10 cc. of sulphuric acid, specific gravity 1.8. By means of cork-lined tongs or test tube holder manipulate the flask over a bare Bunsen flame until most of the free acid is expelled and no sulphur remains on the walls of the flask nor in the liquid. Do not attempt to take to dryness. Place the hot flask on a piece of asbestos. The tin is now all a stannic and the antimony all an antimonous salt. When the flask cools sufficiently add 25 cc. of cold water and 5 cc.² of hydrochloric acid, specific gravity 1.2. Manipulate over a free flame for half a minute to complete the solution of the tin and antimony salts and to expel any sulphur dioxide. Cool the flask under running water. Add 100 cc. of cold water and titrate rapidly with N/20 potassium permanganate. From the volume of the latter required to give the first pink color calculate the per cent. of antimony. Dry to constant weight some highest purity sodium oxalate, made according to Sorensen, and use this to standardize the N/20 potassium permanganate solution.

Tin.—Weigh exactly 0.2 gram of the filings and transfer as before to a 300 cc. Jena Erlenmeyer flask. Add 5 cc. of 15 per cent. sodium carbonate solution. Add 20 cc. of hot water. Add 25 cc. of hydrochloric acid, 1.2 specific gravity. Add one drop of 5 per cent. antimony chloride solution from a dropping bottle. This solution should be strongly acid with HCl . Close the flask with a 1-hole rubber stopper carrying a capillary U-tube of 1 mm. bore. The short arm of the U-tube should just reach through the stopper while the long arm should almost reach the surface on which the flask stands. Place the flask on a hot plate where it will boil very slowly but not suck air back through the tube. The solder will dissolve in about 15 minutes, leaving a small black precipitate of antimony. As soon as this occurs and without interrupting the slow boiling bring a test tube of 15 per cent. sodium carbonate solution under the U-tube. Carry to the sink and cool the flask under running water, allowing the carbonate solution to suck back into it. When cold add 5 cc. of 15 per cent. sodium carbonate solution and 5 cc. of cold, fresh starch liquor and titrate immediately with N/20 iodine solution. From the volume of the latter required to give the first deep blue color calculate the per cent. of tin. Standardize the N/20 iodine solution by titrating in the same way 0.1 gram portions of filings made from a stick of Kahlbaum's highest purity tin.

¹ J. Am. Chem. Soc., 29, 66.

² P. H. Walker and H. A. Whitman also use less hydrochloric acid than A. H. Low, *This Journal*, 1, 519.

This method can be used to advantage for soft solder containing 0 to 2 per cent. of antimony, 30 to 60 per cent. of tin, 40 to 70 per cent. of lead and not more than traces of any other metals. Duplicate determinations of tin and antimony can be made in one hour.

J. H. GOODWIN.

THE USE OF ALUNDUM CRUCIBLES IN FATTY ACID DETERMINATIONS.

Recently the writer has had some opportunities of making separations and determining fatty acids from soaps and soap powders.

These separations were, at first, made by the usual methods, as taking up with beeswax, or upon a balanced filter.

The porous alundum crucibles, manufactured by the Norton Co., were then used as a Gooch crucible, by placing the crucible into a Gooch funnel, using a filtering bottle and a pump for suction.

The method used was by acidifying the soap solution, as usual, with an acid, allowing it to stand for some time, to give the fatty acids enough time to thoroughly coagulate. The solution was then run through this crucible, which was weighed, and the acids remaining in the crucible washed once or twice with cold water. It was then dried and weighed.

The writer finds this method to be very rapid and accurate. When the determinations are completed the fatty acids can be burned out very readily, leaving the crucible as clean as before filtering, and may be used again for a considerable number of determinations.

As the crucible is not acted upon, or contaminating the solutions with any foreign matter, but leaving it in a perfectly clear state, the filtrate passing through may be used for other determinations if so desired.

As this method is found to be more rapid and fully as accurate as the two former methods, also owing to the fact that the crucible can be used for numerous determinations, the writer can say that the use of these crucibles excel any methods, for this separation.

H. O. ANDERSON.

DISSOLVING SILICON ALLOYS.

Editor Journal of Industrial and Engineering Chemistry:

In working on some silicon alloys recently I found they may be readily decomposed by a mixture of strong hydrofluoric with hydrochloric or sulphuric acid.

The alloys so far tried include samples of 50 per cent. ferro-silicon and one of silico-spiegel (21 per cent. Si, 39 per cent. Mn and 42 per cent. Cr). The sample is placed in a large platinum crucible, conc. hydrofluoric acid added and then hydrochloric or sulphuric as desired. The solution starts at once and is complete in a few minutes at a low heat. The sample does not even have to be finely powdered for I have dissolved ordinary crushed ferro-silicon in pieces as large as 10 mesh.

For determination of iron or manganese this method is much more rapid and far simpler than either of the fusion methods.

These facts do not appear to be widely known and are not mentioned in several of the best known books on metallurgical analyses which I have consulted. The ordinary method is to fuse with sodium peroxide in a nickel crucible or with sodium carbonate and potassium nitrate in a platinum crucible. Both these methods have well-known objections which need not be discussed here.

After doing this work in looking up methods for analyses I found that the method of decomposing silicon alloys had been used by at least one concern making ferro-silicon.

But in view of the fact that this method has not been widely published I thought this note might be of interest to the readers of the Journal.

GEORGE C. DAVIS.

THE DETERMINATION OF FREE SULPHUR IN CONDIMENTAL FEEDS, STOCK TONICS AND CONDITIONERS.

In the examination of condimental feeds, stock and poultry tonics, etc., under the recently enacted Condimental Feed Law of North Carolina¹ it was found to be a very important point to know exactly how much free sulphur the various preparations contained. Accordingly, a considerable amount of time was spent in trying various methods for the determination of free sulphur, and as none of them proved entirely satisfactory for the material in hand a method was finally worked out which gave satisfactory results and answered all the requirements for this class of work.

The condimental feeds,² conditioners, etc., to which this method was applied usually consist of a base material, such as wheat bran, middlings, oil meal or cotton-seed meal to which has been added various condiments and drugs. The most common vegetable drugs are pepper, fenugreek, ginger, turmeric, gentian, and licorice. The most common mineral drugs are salt, Glauber's salt, Epsom salts, calcium carbonate, sodium bicarbonate, saltpeter, sulphur, oxide of iron and black antimony. From this it will be seen that a method for determining free sulphur in these preparations must eliminate both the combined sulphur in the base material and the vegetable drugs and the combined sulphur in the mineral drugs in the form of sulphates and sulphides. These difficulties are best overcome by dissolving out the free sulphur by carbon bisulphide, which was used in the method as finally worked out. Quite a number of methods were tried applying them to the original sample and also to the sulphur after it had been extracted with carbon bisulphide. The accuracy of the methods was tested by applying them to a wheat feed to which 10 per cent. flowers of sulphur had been added, and after the present method had been worked out further tests were made with the various methods using the results as checks.

The first method tried was the Pozzi-Escot³ method.

¹ Public Laws of North Carolina, 1909.

² A complete report of this work will be published in a bulletin of this Department at a later date.

³ This method, published in *Rev. gen. chim. Appl.*, April 7, 1904, was used by J. P. Street, New Jersey Expt. Sta. *Bull.* No. 184, and the general procedure was very kindly furnished the author in a personal communication.

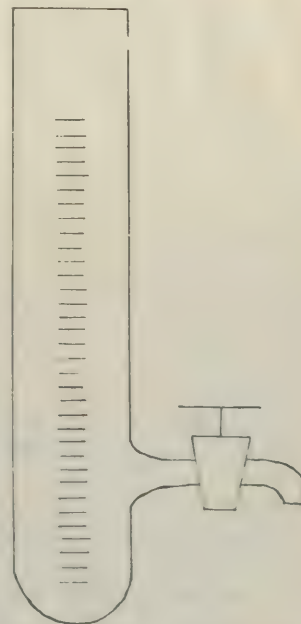
This method depends on the oxidation of the sulphur by chromic acid. Unsatisfactory results were obtained when the method was tried on flowers of sulphur and a composite sample so that it was not tested further.

The Avery¹ method for determining sulphur in insecticides was tried out fully. This method consists, briefly, in putting the sulphur in solution in sodium hydroxide solution (100 grams in 100 cc. water), then oxidizing with hydrogen peroxide and precipitating the sulphates with barium chloride. When applied to the composite sample and to two stock tonics of varying composition this method gave results too low to permit its being used. When applied to the sulphur extracted from these samples by carbon bisulphide the results were nearer correct, but were still too low. In this case the low results were attributed to the error introduced by the frothing of the solution and not to incomplete oxidation.

Oxidation with bromine was then tried in a somewhat similar manner to Eschka's² method for determining sulphur in coal. The sulphur was first taken up with sodium hydroxide solution and then oxidized by treating with saturated bromine water and the sulphates precipitated with barium chloride. This gave low results both on the original sample and the sulphur extracted from the samples.

Oxidation with chlorine gas, according to the method of Rivot, Beudant and Daguin,³ when applied to the original samples gave high results. Further tests showed that the high results were caused by the oxidation of part of the sulphur of the base material.

The method as finally worked out is as follows: One gram of the sample is weighed into a side neck tube (see figure), 50 cc. carbon bisulphide added, the tube stoppered tightly, placed in a shaking machine and shaken for five hours. The tube is then taken out of the machine and allowed to stand overnight, thus giving a perfectly clear solution. 20 cc. of the solution = 0.4 gram of the sample are then drawn off, by means of the side neck, into a flask, the carbon bisulphide evaporated off and the flask dried in a water oven. The sulphur is then taken up with sodium hydroxide solution as in the Avery method, the solution diluted and the sulphur oxidized by passing in a stream of chlorine, the solution made acid and heated to expel chlorine, filtered and the sulphates precipitated with barium chloride. On



¹ Bureau of Chemistry, *Bull.* 90 and *Bull.* 107 (revised).

² *Z. anal. Chem.*, 13, 344. Fresenius "Quant. Anal.," Vol. II, revised, 1908.

³ Fresenius "Quant. Anal.," Vol. I, revised, 1908.

the composite sample containing 10 per cent. sulphur this method gave 9.94 per cent. sulphur. Several duplicates made at the same time gave closely agreeing results. A number of determinations on stock tonics of varying composition gave satisfactory results with closely agreeing duplicates.

The side neck tubes used in the method, shown in the figure are heavy graduated glass tubes 16.4 cm. tall and 3.0 cm. in diameter with a side neck carrying a stopcock fused in about 5.0 cm. from the bottom of the tube. The use of this side neck was found to be the most satisfactory means of drawing out the aliquot portion. When the tubes are put in the shaking machine they are closed with tight-fitting cork stoppers. No trouble has been experienced by evaporation from this source. Settling the suspended particles in the tube by means of a centrifugal machine was tried, but with only a fair amount of success and it was found better, when time will permit, to allow the tubes to stand overnight before drawing off the aliquot, thus giving a perfectly clear solution. It was found most satisfactory to draw off the aliquot into an Erlenmeyer flask of about 450 cc. capacity. Then during the oxidation with chlorine the flask is closed with a two-hole stopper. One hole is used for the tube from the generator and the other is used for a waste tube to carry off the excess of chlorine gas.

G. M. MACNIDER.

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A COMPARISON BETWEEN THE REFRACTION AND THE SPECIFIC GRAVITY OF MILK SERUM FOR THE DETECTION OF ADDED WATER.

It is oftentimes very difficult for the food chemist to distinguish between honest low-standard milk and fraudulently watered milk. Various methods have been suggested, most of them being more or less unsatisfactory, owing to the time involved and difficulty of analysis, variability of the milk constants, and the consequent unreliability of results. It has been found that the milk serum possesses a fairly constant composition, more so than the milk itself.

Different methods have been used for precipitating the casein and obtaining the serum. G. Wiegner and G. Yakuwa, of Goettingen University,¹ use a dilute solution of CaCl_2 to obtain the serum. The "Specific Refraction," an arbitrary constant, is then determined. Ackermann² also uses CaCl_2 to precipitate the casein and determine the refraction of the serum, claiming that it varies less than serum obtained by any other method. C. Mai and S. Rothenfusser,³ also use the CaCl_2 method, claiming they can detect four per cent. of water. The natural souring method is used by Matthes and Nuller,⁴ who get very uniform results.

¹ "The Extent of Refraction and Specific Gravity of Calcium Chloride Serum of Milk," *Milchwirtsch. Zentr.*, **5**, 473.

² "The Refractometric Detection of Added Water in Milk," *Z. Nahr.-Genuss.*, **16**, 586.

³ "The Refraction of Calcium Chloride Milk Serum," *Z. Nahr.-Genuss.*, **18**, 737.

⁴ "Über die Untersuchung des Milch Serums mit dem Zeiss'schen Eintansch-Refraktometer," *Z. für öffent. Chem.*, **3**, 173.

The "Asaprol Method" is used by Baier and Neumann, but, owing to the dilution of the serum, is not regarded by some as accurate. Leach,¹ and Lythgoe and Nurenberg,² express preferences for the acetic acid method. As it is the method used in the following determinations, it is described in detail. To 100 cc. of milk add 2 cc. of 25 per cent. acetic acid (sp. gr. 1.035). Heat at 70° C. for 20 minutes in a beaker covered with a watch glass on the water bath. Then cool for 10 minutes in ice water and filter. If the first part of the filtrate is cloudy, it will usually clear up if refiltered through the same filter paper.

The serum being obtained in the above manner, the refraction at 20° C. is determined by the Zeiss immersion refractometer and the specific gravity at 15° C. by the Westphal balance accurately graduated to four places.

As a preliminary, the refraction and fat content of different milk samples from individual cows were determined, the fat being determined by the Babcock method.

TABLE 1.

Milk.	Refraction.	Per cent. fat.
Holstein, pure bred.....	39.8	3.4
Holstein, pure bred.....	39.2	3.4
Holstein, pure bred.....	43.0	3.0
Guernsey, pure bred.....	42.5	...
Guernsey, pure bred.....	47.3	4.7
Guernsey, pure bred.....	44.8	5.2
Guernsey, pure bred.....	42.7	3.3
Red Poll, pure bred.....	43.8	3.7
Red Poll, pure bred.....	41.9	6.2
Red Poll, pure bred.....	43.5	...
Jersey, pure bred.....	44.8	5.0
Jersey, pure bred.....	45.5	4.8
Angus, pure bred.....	43.2	4.2
Angus, pure bred.....	43.4	3.5
Short Horn, pure bred.....	44.0	4.1
Short Horn, pure bred.....	42.0	4.3
Devon, pure bred.....	43.2	4.6
Kerry, pure bred.....	42.7	5.2
Grade Red Poll, pure bred.....	41.3	4.4
Average.....	43.1	4.3
Highest (Guernsey).....	47.3	(Red Poll) 6.2
Lowest (Holstein).....	39.2	(Holstein) 3.0

This table shows variation in refraction from 39.2 to 47.3 and also shows there is no relation between the refraction and the fat content in the sample used.

Table 2 shows that milk serum from the same cow will vary in refraction if taken at different times. Hence it would seem impossible to estimate absolutely the amount of added water in a sample even when the original source of the milk is known unless the milk came from a large herd when it might be possible as the composite serum will vary less than the individual serum.

TABLE 2.

Milk.	First sample.	Two weeks later.
Guernsey.....	44.8	43.7
Holstein.....	39.2	40.8
Holstein.....	39.8	41.2
Short Horn.....	44.0	44.1
Guernsey.....	47.3	42.2
Red Poll.....	43.8	43.9
Angus.....	43.4	43.9

Table 3 shows milk systematically adulterated

¹ "Food Inspection and Analysis."

² "A Comparison of Methods for the Preparation of Milk Serum," *THIS JOURNAL*, **1**, 38.

and shows the decrease in refraction and specific gravity as water is added.

TABLE 3

Milk "A"	Refraction at 20° C.	Sp. gr. at 15° C.
0 per cent. H ₂ O.....	41.9	1.0292
5 per cent. H ₂ O.....	40.3	1.0269
10 per cent. H ₂ O.....	39.4	1.0262
15 per cent. H ₂ O.....	38.4	1.0247
20 per cent. H ₂ O.....	36.6	1.0233
Milk "C"		
0 per cent. H ₂ O.....	43.7	1.0313
5 per cent. H ₂ O.....	42.2	1.0285
10 per cent. H ₂ O.....	41.4	1.0280
15 per cent. H ₂ O.....	39.4	1.0262
20 per cent. H ₂ O.....	38.8	1.0251
25 per cent. H ₂ O.....	36.5	1.0234
Milk "D"		
0 per cent. H ₂ O.....	40.8	1.0275
5 per cent. H ₂ O.....	38.9	1.0247
10 per cent. H ₂ O.....	37.4	1.0237
15 per cent. H ₂ O.....	35.8	1.0224
20 per cent. H ₂ O.....	34.3	1.0205
25 per cent. H ₂ O.....	33.8	1.0195
Milk "E"		
0 per cent. H ₂ O.....	43.0	1.0280
5 per cent. H ₂ O.....	40.7	1.0263
10 per cent. H ₂ O.....
15 per cent. H ₂ O.....	39.3	1.0243
20 per cent. H ₂ O.....	37.0	1.0220
25 per cent. H ₂ O.....	35.9	1.0209
Milk "F"		
0 per cent. H ₂ O.....	41.2	1.0320
5 per cent. H ₂ O.....	39.6	1.0259
10 per cent. H ₂ O.....	37.9	1.0231
15 per cent. H ₂ O.....	36.2	1.0219
20 per cent. H ₂ O.....	35.9	1.0202
Milk "G"		
0 per cent. H ₂ O.....	44.2	1.0306
5 per cent. H ₂ O.....	41.2	1.0277
10 per cent. H ₂ O.....	39.4	1.0251
15 per cent. H ₂ O.....	38.7	1.0238
20 per cent. H ₂ O.....	36.4	1.0220
25 per cent. H ₂ O.....	35.8	1.0217

The average decrease in refraction due to every 10 per cent. of added water is 2.7. The average refraction of all the pure samples used is 42.8, the refraction of water 15.0. By a mathematical calculation it is determined that 10 per cent. added water should lower the refraction 2.8, corresponding very closely with the results found.

100 per cent. milk.....	42.8
100 per cent. H ₂ O.....	15.0
90 per cent. milk.....	38.5
10 per cent. H ₂ O.....	1.5
90 per cent. milk, 10 per cent. H ₂ O.....	40.0
42.8 — 40.0 = 2.8, decrease due to 10 per cent. water.	

The average decrease in specific gravity due to every 10 per cent. added water is 0.0031. The average specific gravity of all pure samples is 1.0291 at 15° C. The specific gravity of water at 15° C. is 0.9991. By calculation it is determined that 10 per cent. of added water should decrease the specific gravity of the serum 0.0030, corresponding within 0.0001 of the results found.

100 per cent. milk.....	1.0291
100 per cent. H ₂ O.....	0.9991
90 per cent. milk.....	0.92619
10 per cent. H ₂ O.....	0.09991
90 per cent. milk, 10 per cent. H ₂ O.....	1.0261
1.0291 — 1.0261 = 0.0030	

Woodman¹ finds that 10 per cent. added water lowers the specific gravity of the serum 0.0031 and

attempts to show that he can accurately estimate the amount of water added by taking that figure. Owing to the variability of the specific gravity of various milk serums it would not seem feasible. The pure samples examined by the author vary from 1.0270 to 1.0320.

Radulescu¹ and König² both state that 10 per cent. of added water decreases the specific gravity of the serum 0.0003–0.0010. All other results point toward 0.0031 as nearer the exact figure.

Most authorities take the lowest limit of refraction for pure milk serum as 39.0 regarding samples under 40.0 as suspicious. This corresponds to the results found by the author. Two Holstein samples were found under 40.0 but it is very unlikely that the composite milk of the herd, even of Holsteins, would run under 40.0. Of fourteen systematically adulterated, individual samples, 5 per cent. added water (by volume) was distinguishable in four cases, taking 39.0 as the limit of pure milk, and the milk would be regarded as "suspicious" in three more cases. 10 per cent. added water was distinguished in six cases and was "suspicious" in three cases. 15 per cent. added water is distinguishable in nine cases and was "suspicious" in five cases. 20 per cent. added water was distinguishable in every sample.

1.0270 is regarded by most authorities as the low limit for the specific gravity of pure milk serum at 15° C. Leach and Lythgoe³ present figures showing pure Holstein milk running as low as 1.0253 but in every case the milk itself had a specific gravity under the legal standard, 1.0290. The author has been unable to find any other authorities presenting authentic figures as low. Milks "M" and "N" were taken from the first milkings of Holstein cows but did not run under the limit, 1.0270. Hence, 1.0270 has been taken as the low limit for pure milk serum.

The specific gravity of the serums of the 14 individual samples (Table 3, part) was determined on the same serum as the refraction, with the result that 5 per cent. added water is distinguishable in 8 cases. 10 per cent. added water is distinguishable in twelve cases and 15 per cent. of water in fourteen cases.

From the above results it would appear that the specific gravity of the serum is a much more delicate test for added water than the refraction, but owing to the fact that all authorities are not agreed as to the low limit of the specific gravity of pure milk serum, the author would say that it is not as reliable in all cases as the refraction. Both methods combined should furnish both a delicate and reliable guide to the detection of added water in milk. As both the methods may be used on the same serum, and as the determinations are easily made after the serum has been obtained, it appears that a combination of the two methods would insure the certain

¹ "Mitl. ans dem pharm. Ins. und Laboratorium für ang. chem. der Univ. Erlangen (1890)" 3, 93.

² "Die Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe," Ed. (1898), 36.

³ "The Detection of Watered Milk," *J. Am. Chem. Soc.*, 26, 1195 (1904).

¹ *J. Am. Chem. Soc.*, 21, 503 (1899).

detection of added water, if in any quantity as would be used in fraudulently adulterated milk.

SLEETER BULL.

OHIO STATE UNIVERSITY,
COLUMBUS, OHIO.

BOOK REVIEWS AND NOTICES.

High Speed Steel. The Development, Nature, Treatment, and Use of High Speed Steels, together with some suggestions as to the Problems Involved in Their Use. By O. M. BECKER, Industrial Engineer. Cloth, pp. v + 344. McGraw-Hill Book Company, 1910. Price, \$4.00 net.

A very good book from both practical and theoretical standpoints. In a general way the development of high-speed steel and the marvelous advance it has caused in machine operation and output are known, but one begins to understand the real magnitude of that advance, as he turns the pages of this book.

The first chapters give a short history of the development of metal cutting from earliest times and methods of manufacture of the ancient steels, including the famous Wootz and Damascus brands, the later crucible, open-hearth, Bessemer and electric furnace processes, relate the discovery of Mushet—the forerunner of the high-speed steels, and the extensive experiments of Taylor and White which resulted in the wonderful steels which we have to-day. Tables are given of the chemical composition of the various types, and their properties and requirements for hardening explained according to the latest and accepted theories of metallurgy. The author has had the aid of such well-known metallurgists as Carpenter, Taylor, Stoughton, and others, in ways of suggestion, criticism, use of material, proof-reading, etc. The metallographical explanations and photomicrographs are good and make clear the theories.

The balance and larger part of the book is devoted to the practical part of the subject: the making of the steel, forging the tools, hardening, tempering, annealing, grinding, etc. The descriptions of the various types of hardening and annealing furnaces, pyrometers, machines, etc., are very complete, and apparently no usable type is omitted. Chapters are given on speeds and feeds, new requirements for machines, notes on remodeling old equipment and the problems involved. The book is well illustrated. In the appendix are given several practical tables. The volume should be of much assistance to the superintendent, metallurgist or practical tool man.

I. M. BREGOWSKY,
L. W. SPRING.

Der Kautschuk und seine Prüfung. By F. W. HINRICHSSEN and K. MEMMLER. 8vo, pages x + 263. Leipzig: S. Hirzel, 1910. Price: Paper, 8 marks; cloth, 9 marks

This is, doubtless, the most comprehensive work that has been published up to date on rubber and is particularly valuable in the rubber industry to those interested in the physical testing of vulcanized rubber. A glance over the table of contents gives the

best idea of the scope and thoroughness with which the work has been carried out. (I) *General Part*, by F. W. Hinrichsen. (A) Introduction, (B) Occurrence of Rubber, (C) Properties of the Latex, (D) Constitution of the Rubber Hydrocarbon, (E) Other Substances Associated with the Rubber Hydrocarbon in Crude Rubber, (F) Physical Properties of Crude Rubber, (G) Chemical Properties of Crude Rubber, (H) Theory of Vulcanization of Rubber, (I) Technical Handling of Rubber Materials, (J) The Properties of Vulcanized Rubber. (II) *Chemical Analysis of Rubber*, by F. W. Hinrichsen. (A) Analysis of Crude Rubber, (B) Analysis of Vulcanized Rubber, (C) Life Tests of Finished Rubber Articles. (III) *Mechanical Testing of Rubber*, by K. Memmler. (A) The Practical Carrying Out of Strength Tests on Soft Rubber. (B) Results of Strength Tests on Soft Rubber according to the Older and More Recent Publications.

The authors have compiled and arranged very excellently the work of the older and modern investigators in the field of rubber testing. Of particular interest is the attention given to the physical testing of vulcanized rubber, a division of the subject in most other works that has been given but slight attention. Nevertheless, from the standpoint of our knowledge of rubber as a material of construction it is one of the most important. The discussion of tensile tests, the pressure tests, the machines and apparatus, the elongation curves, the hysteresis curves, is very admirably written.

W. C. GIN.

Die Chemie der Cellulose. By CARL G. SCHWALBE. First Half. 8vo. pp. 272. Berlin: Gebrüder Borntraeger, 1910.

This work is unquestionably the best on the chemistry of cellulose which has as yet been published. While it is largely bibliographic in its text, its construction and method of handling is excellent. This first half deals with cotton cellulose as a type, and considers its behavior and relation towards water, heat, alkalis, acids, salts, dyes, oxidation and reducing agents, solvents and ferments. The cellulose products produced by hydrolysis and oxidation are treated at some length. The conclusion of the first half commences the consideration of the esters of cellulose which, as stated, are to be handled fully in the second half to be published very soon.

H. S. MORK.

Die Unterscheidung der Natürlichen und Künstlichen Seiden. By DR. ALOIS HERZOG. Paper, 12mo., pp. 78. Dresden: Theodor Steinkopff, 1910. Price, 75 cents.

This small pamphlet, containing fifty excellent microphotographs and illustrations, treats in a full and complete manner of the methods of differentiating the various artificial silks from each other and from the natural product. While both chemical and optical methods are given, the latter receive the greater attention. Excellent photographs are shown of the appearance of the fibers under the ultramicroscope at a magnification of 2500.

H. S. MORK.

Testing for Metallurgical Processes. By JAMES A. BARR. 12mo. Cloth, pp. 208. San Francisco: Mining and Scientific Press, 1910. Price, \$2.00.

This book is based upon notes and experiments made by the author, while instructor at the Michigan College of Mines, and aims to describe laboratory experiments and methods of testing ores which will enable the student to secure definite data upon which to base an opinion as to the most available method for the extraction of a metal from its ore. It deals with the ores of gold, silver, copper and zinc, and describes the principles upon which depend the effective application of the various well-known processes, including amalgamation, chlorination, cyanidation, roasting, refining of lead bullion, zinc smelting, and smelting of lead silver ores. An interesting chapter on the properties of slags is especially worthy of mention. The illustrations of this book are simple and clear. The book presupposes at least an elementary knowledge of chemistry, but its style is extremely practical. This publication should prove of value not only to students but also to those interested in the mining or the treatment of the metals mentioned.

WM. HOSKINS.

Practical Stamp Milling and Amalgamation. By H. W. McFARREN. 12mo. Cloth, pp. 165. San Francisco: Mining and Scientific Press, 1910. Price, \$2.00.

This is a practical book and does not pretend to be anything else. The author has evidently told what he has learned in the practice of milling and amalgamation, and tells it as one who knows little of the subject would like to have it told, in sufficient detail. The book can be recommended to those employed in the stamp mill or having to do with the treatment of gold ores by the ordinary milling processes. The book is particularly valuable to a person about to engage in the mining or milling of gold ores.

WM. HOSKINS.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

ASSOCIATION OF FEED CONTROL OFFICIALS.

The second annual meeting of the Association of Feed Control Officials was held at the Raleigh Hotel, Washington, D. C., November 14-16th. There were in attendance at the meeting some eighty feed control officials, manufacturers and their representatives, representing practically all sections of the United States and all phases of the feeding-stuff trade.

The most important subject before the convention was the adoption of a draft for a uniform feeding-stuff law for the states and uniform definitions.

The program was carried out as follows:

FIRST DAY—MORNING SESSION.

Monday, November 14, 1910, 10 o'Clock.

Raleigh Hotel, Washington, D. C.

1. Convention called to order by the President, Benj. L. Purcell, Virginia.
2. Roll Call.
3. Appointment of Committees.
4. President's Address—Benj. L. Purcell, Virginia.
5. Report of Executive Committee—L. F. Brown, *Chairman*, New York.
6. Report of Committee on Credentials.
7. New Business.

Recess.

AFTERNOON SESSION. 2 o'Clock.

Discussion of that part of report of Executive Committee relating to Uniform Law and Definitions for Feeds.

By Feeders, Individual Manufacturers and Representatives of Trade Associations.

Executive Session

SECOND DAY—MORNING SESSION.

Tuesday, November 15, 1910, 10 o'Clock.

1. Reports of Committees.
2. Address—Importance of Making Feed out of Sound Material—Dr. H. W. Wiley, Chief U. S. Bureau Chemistry.
3. Address—Coöperation between Feed Dealer and Executive of the Law—Dr. C. D. Woods, Maine.
4. Address—The Manufacturers' Position and Needs—Robt. W. Chapin, Buffalo, N. Y.
5. Discussion of the above addresses.
6. Unfinished Business.

SECOND DAY—AFTERNOON SESSION. 2 o'Clock.

EXECUTIVE SESSION.

Discussion of Uniform Feeding Stuff Law and Definition for Feeds.

Open to Members of this Association only.

THIRD DAY.

Wednesday, November 16, 1910, 10 o'Clock.

1. Reports of Committees.
2. Continued discussion of a Uniform Feeding-Stuff Law and Definitions for Feeds.
3. Election of Officers and Executive Committee for ensuing year.
4. Unfinished business.

Adjournment.

The meeting was a very profitable and valuable one to all concerned and resulted in definite steps being taken toward the adoption of a uniform law. After a full and free discussion by the feed control officials and manufacturers present, the draft for a proposed uniform law (see below) was adopted. On motion the Committee on Definitions was continued. Definitions prepared by the committee covering some fifty terms used in the feeding-stuff trade were tentatively adopted and ordered published for the information of the trade and to elicit criticism. The Executive Committee was instructed to consider the advisability of amalgamating with some other association engaged in work similar to that of the feed control. The report of the Nominating Committee was unanimously adopted and the following officers were elected:

President, L. F. Brown, New York; *Vice-President*, W. P. Hand, Mississippi; *Secretary and Treasurer*, J. D. Turner, Kentucky; *Executive Committee*, W. D. Woods, Maine, J. K. Haywood, U. S. Department of Agriculture, and W. J. Jones, Jr., Indiana.

Association adjourned at noon, November 16th, subject to call of Executive Committee.

PROPOSED UNIFORM FEED LAW.

SECTION 1.—The term "Commercial Feeding-Stuffs" shall be held to include all feeding-stuffs used for feeding live stock and poultry, except whole seeds or grains; the unmixed meals made directly from the entire grains of corn, wheat, rye, barley, oats, buckwheat, flaxseed, kaffir and milo; whole hays, straws, cottonseed hulls and corn stover when unmixed with other materials. Together with all other materials containing 60 per cent. or more of water.

SEC. 2.—Every lot or parcel of commercial feeding-stuffs sold, offered or exposed for sale or distributed within this state shall have affixed thereto a tag or label, in a conspicuous place on the outside thereof, containing a legible and plainly printed statement in the English language, clearly and truly certifying:

- (a) the net weight of the contents of the package, lot or parcel;
- (b) the name, brand or trade mark;
- (c) the name and principal address of the manufacturer or person responsible for placing the commodity on the market;

- (d) the minimum per centum of crude protein;
- (e) the minimum per centum of crude fat;
- (f) the maximum per centum of crude fiber;
- (g) the specific name of each ingredient used in its manufacture.

The crude protein, crude fat and crude fiber shall be determined by the methods in force at the time by the Association of Official Agricultural Chemists of the United States.

SEC. 3. Before any manufacturer, importer, jobber, firm, association, corporation or person shall sell, offer or expose for sale or distribute in this state any commercial feeding-stuffs, he or they shall file with.....a certified copy of the statement specified in Section 2 for each brand of commercial feeding stuffs; said certified copy to be accompanied, when theshall so request, by a sealed package containing at least one pound of the commercial feeding-stuffs to be sold, offered or exposed for sale or distributed in this state, and the company or person furnishing said sample shall thereupon make affidavit that the said sample is representative of the commercial feeding-stuffs offered for registration.

SEC. 4.—(The provisions of this section are proposed for the benefit of those states who may not secure a direct appropriation from the legislature to cover the expenses enforcing the law.) Each and every manufacturer, importer, jobber, firm, association, corporation or person manufacturing or selling any commercial feeding-stuffs as defined in Section 1 of this act shall pay to the.....an inspection tax or fee of.....per.....for each brand of commercial feeding-stuffs sold, offered or exposed for sale or distributed in this state, and shall affix to, or accompany, each lot shipped in bulk, and to each parcel of such commercial feeding-stuffs a tag, stamp or label to be furnished by the.....stating that all charges specified in this section have been paid. Whenever any commercial feeding-stuff as defined in Section 1 is offered or exposed for sale in bulk or otherwise stored, the manufacturer, importer, jobber, firm, association, corporation or person keeping the same for sale shall keep on hand cards upon which shall be printed the statement required by the provisions of Section 2, and when such feeding-stuff is sold at retail in bulk or in packages belonging to the purchaser, the manufacturer, importer, jobber, firm, association, corporation or person shall furnish the purchaser with sufficient tax tags or stamps to cover the sale, and, upon request, with a card or cards upon which appears the statement required by the provisions of Section 2.

SEC. 5.—The.....shall have power to refuse to register any commercial feeding-stuffs under a name, brand or trade mark which would be misleading or deceptive, or which would tend to mislead or deceive as to the materials of which it is composed, or when the specific name of each and all ingredients used in its manufacture are not stated. He shall also have the power to refuse to register more than one commercial feeding-stuff under the same name or brand when offered by the same manufacturer, importer, jobber, firm, association, corporation or person. Should any commercial feeding-stuffs be registered in this state, and it is afterward discovered that such registration is in violation of any of the provisions of this act, the.....shall have the power to cancel such registration. The.....shall have the power to refuse to allow any manufacturer, importer, jobber, firm, association, corporation or person to lower the guaranteed analysis or change the ingredients of any brand of his or their commercial feeding-stuffs during the term for which registered, unless satisfactory reasons are presented for making such change or changes.

SEC. 6.—Whenever a manufacturer, importer, jobber, firm, association, corporation or person manufacturing or selling a

brand of commercial feeding-stuffs shall have filed the statement required by Section 3, and paid the inspection tax or fee, as required by Section 4, of this act, no other agent, importer, jobber, firm, association, corporation or person shall be required to file such statement or pay such tax or fee upon such brand.

SEC. 7.—The.....is authorized in person or by deputy to have free access to all places of business, mills, buildings, carriages, cars, vessels, and parcels of whatsoever kind used in the manufacture, transportation, importation, sale or storage of any commercial feeding-stuffs, and shall have the power and authority to open any parcel containing or supposed to contain any commercial feeding-stuffs, and upon tender and full payment of the selling price of said sample, to take therefrom, in the manner prescribed in Section 8, samples for analysis, and saidshall annually cause to be analyzed at least one sample so taken of every commercial feeding-stuff that is found sold, offered or exposed for sale or distributed in this state.

SEC. 8.—A representative sample of each brand of commercial feeding-stuffs found, sold, offered or exposed for sale shall be taken by the said.....or his duly authorized representative in the presence of at least one witness. No action shall be maintained for a violation of the provisions of this act, based upon an analysis of a sample from less than five separate original packages, unless there be less than five separate original packages in the lot, in which case portions for the official sample shall be taken from each original package; if the commercial feeding-stuffs are in bulk, portions shall be taken from not less than five different places in the lot, provided that this does not exclude sampling in bulk when not exposed sufficiently to take portions from five different places, in which case portions are to be taken from as many places as practicable. If the sample thus secured is larger than is required, it shall be mixed and quartered until a sample of suitable size remains. Said sample shall be divided into two parts, and shall be placed in packages and sealed in the presence of said witness; one of said packages so sealed shall be tendered, and if accepted, delivered to the person apparently in charge of such feeding-stuffs; the other package the said.....shall analyze or cause to be analyzed and the result, of such analysis, together with such additional information as the said.....may deem advisable, shall be promptly transmitted to the manufacturer or person responsible for the placing of the commodity on the market, and shall be published in reports or bulletins from time to time. If the manufacturer or person responsible for the placing of any commodity so sampled upon the market be unable to secure the sample delivered to the person apparently in charge of the feeding-stuffs sampled, he shall upon request to thebe furnished with a portion of the official sample referred to in this section. The methods of analysis shall be those in force at the time by the Association of Official Agricultural Chemists of the United States.

SEC. 9.—If it appear that any of the provisions of this act has been violated, the.....shall certify the facts to the proper prosecuting attorney and furnish that officer with a copy of the results of the analysis or other examination of such feeding-stuffs duly authenticated by the analyst or other officer making the determination, under the oath of such officer, provided that if it shall appear from any such examination that any of the provisions of this act have been violated the.....shall cause notice to be given to the manufacturer or dealer from whom said sample was taken; any party so notified shall be given an opportunity to be heard in his defense under such rules and regulations as may be prescribed by thebefore the facts shall be certified to the proper prosecuting attorney. In all prosecutions arising under the provisions of this act, certificates of the analyst or

other officer making the examination or analysis, when duly sworn to by such officer, shall by *prima facie* evidence of the fact or facts therein certified.

SEC. 10.—Any manufacturer, importer, jobber, firm, association, corporation or persons who shall sell, offer or expose for sale, or distribute in this state, any commercial feeding-stuffs without having attached thereto or furnished therewith such tax stamps, labels or tags as required by the provisions of this act, or who shall use the required tax stamps, labels, or tags a second time, or use a counterfeit of such tax stamps, labels, or tags, or who shall impede, obstruct, hinder or otherwise prevent or attempt to prevent said.....or his authorized agent in the performance of his duty in connection with the provisions of this act, or who shall sell, offer or expose for sale or distribute in this state any commercial feeding-stuffs as defined in Section 1, without complying with the requirements of the provisions of this act, or who shall sell, offer or expose for sale or distribute in this state any commercial feeding-stuffs which contain a small per centum of crude protein or crude fat or a larger per centum of crude fiber than is certified to be contained therein, or who shall fail to properly state the specific name of each and every ingredient used in its manufacture shall be deemed guilty of a violation of the provisions of this act and upon conviction thereof shall be fined not more than one hundred dollars (\$100.00) for the first violation and not less than one hundred dollars (\$100.00) for each subsequent violation. Any manufacturer, importer, jobber, firm, association, corporation or person who shall mix or adulterate any feeding-stuffs with any substance or substances injurious to the health of live stock or poultry shall be deemed guilty of a violation of the provisions of this act, and in addition to the penalty provided in this section, the lot of feeding-stuffs shall be subject to seizure, condemnation and sale as the court may direct, the proceeds from such sale to be covered into the state treasury. The court may in its discretion release the feeding-stuffs so seized when the requirements of the provisions of this act have been complied with, and upon payment of all costs and expenses incurred by the state in any proceedings connected with such seizure. (Proceedings in *rem*..... Seizure of goods believed to be shipped or sold in violation of law does not work a forfeiture of them; this can only be declared by a court of competent jurisdiction. The general rule is that a court proceeding in *rem* must have the custody of the *res* in order to pronounce a valid judgment. The goods cannot be condemned without giving the defendant opportunity to be heard. He is not entitled to personal notice before the court can adjudge a forfeiture of his property, but he must have noticed, either actual or constructive, or the proceeding will be void. The title to property as to which an act of forfeiture has been committed is not divested *co instanti* by the offense, but only by the judgment or decree of a court having jurisdiction; and if after the seizure possession is abandoned and forfeiture not decreed, the title and right of possession is in the original owners.

Legal advice to committee is to the effect that no addition can be made to proposed law which would satisfactorily meet the requirements of different states relative to proceedings in *rem*. Some states will require no additional legislation. States which will require additional legislation must so word such legislation as to meet the requirements of the different conditions existing in each individual state.

SEC. 11.—The.....is hereby empowered to enforce the provisions of this act and to prescribe the form of tags, stamps or labels to be used to show that the inspection tax or fee has been paid, and to prescribe and enforce such rules and regulations relating to the sale of commercial feeding-stuffs as he may deem necessary to carry into effect the full intent and meaning of this act.

SEC. 12.—All laws or parts of laws in conflict with the provisions of this act are hereby repealed.

The following resolution was presented by the Committee of the Whole and adopted by the Association.

"This committee report to the convention that they recommend that the Committee on Definitions be continued one year and that these tentative definitions be published as they stand to-day, for the information of the trade and to elicit criticism."

Meal is the clean, sound, ground product of the entire grain, cereal or seed which it purports to represent, provided, that the following meals, qualified by their descriptive names, are to be known, as *viz.*, *corn germ meal* is a product in the manufacture of starch, glucose and other corn products and is the germ layer from which a part of the corn oil has been extracted. *Cottonseed meal* is the meal obtained from the cottonseed kernel after extraction of part of the oil and contains not less than 38.50 per cent. of crude protein. *Linseed meal* is the ground residue after extraction of part of the oil from ground flax seed. *Bolted corn meal* is the entire ground product of corn, bolted.

Grits are the hard, flinty portions of Indian corn.

Hominy meal, feed or chop is the bran coating and germ of the corn kernel and may contain a part of the starchy portion of the kernel.

Corn feed meal is the siftings obtained in the manufacture of cracked corn and table meal made from the whole grain.

Gluten meal is a product obtained in the manufacture of starch and glucose from corn and is the flinty portion of the kernel which lies in its outer circumference just beneath the hull. If the meal is derived from any other cereal, the source must be designated.

Corn bran is the outer coating of the corn kernel.

Gluten feed is a product obtained in the manufacture of starch and glucose from corn and is a mixture of gluten meal and corn bran to which may be added the residue resulting from the evaporation of the so-called "steep-water." If derived from any other cereal, the source must be designated.

Wheat bran is the coarse outer coating of the wheat berry.

Shorts or standard middlings are the fine particles of the outer bran as well as the inner or "bee-wing" bran separated from the wheat bran and white middlings.

Shipstuf or wheat mixed feed is a mixture of the by-products from the milling of the wheat berry.

White wheat middlings are that part of the offal from wheat left after separating it from the bran and the shorts or standard middlings.

Red dog is a low-grade wheat flour containing the finer particles of bran.

Oat groats are the kernels of the oat berry with the hulls removed.

Oat shorts or oat middlings are the starchy portion of the oat groats obtained in the milling of rolled oats.

Oat hulls are the outer covering of the oat grain.

Oat clippings are the small hairs, dust and ends of oats separated from the oats in the clipping process and may contain light oats and oat hulls.

Rice bran is the inner cuticle of the rice hull.

Rice polish is the flour secured from the surface of the rice kernels in polishing.

Rice meal or flour is the clean ground rice.

Rice hulls are the outer covering of the rice grain.

Flax seed meal is the entire flax seed ground.

Flax plant refuse is the flax shives, flax pods, inferior flax seeds and the woody portion of the flax plant or any of the above materials.

Buckwheat shorts or middlings are that portion of the buck-

wheat grain immediately inside of the hull after separation from the flour.

Blood meal is finely ground dried blood.

Meat meal is finely ground beef scraps. If it bears a name descriptive of its kind, composition or origin, it must correspond thereto.

Cracklings are the residue after extracting the fats and oils from the animal tissue. If it bears a name descriptive of its kind, composition or origin, it must correspond thereto.

Digester tankage is meat scraps from edible carcasses which have been inspected and passed as satisfactory for human consumption, especially prepared for feeding purposes through tanking under live steam, drying under high heat and suitable grinding.

Distillers' dried grains are the dried residue from cereals obtained in the manufacture of alcohol and distilled liquors. The product shall bear a designation indicating the cereal predominating.

Brewers' dried grains are the dried residue from cereals obtained after "mashing and sparging" the malt.

Malt sprouts are the sprouts of the barley grain. If the sprouts are derived from any other mated cereal, the source must be designated.

Cottonseed feed shall be a mixture of cottonseed meal and cottonseed hulls containing less than 38.50 per cent. of crude protein and shall be plainly marked "mixture of cottonseed meal and cottonseed hulls."

Alfalfa meal is the entire alfalfa hay ground and does not contain an admixture of ground alfalfa straw or other foreign materials.

Chop is a ground or chop feed composed of one or more different cereals or by-products thereof.

Screenings are the smaller imperfect grains, weed seeds and other foreign materials having feeding value, separated in cleaning the grains. They shall be designated by the name of the seed from which they are derived.

Barley bran is a misnomer.

Cottonseed bran is a misnomer.

Elevator feed is a misnomer.

Cottonseed meal feed is a misnomer.

Cottonseed feed meal is a misnomer.

Oat feed is a misnomer unless applied to whole ground oats.

Flax seed is a misnomer unless applied to whole ground flax seed.

Flax bran is a misnomer.

Oat nubbins is a misnomer.

Buckwheat feed consisting of buckwheat middlings and hulls is a misnomer.

Gluten feed as applied to distillers' grains is a misnomer.

LAKE MICHIGAN WATER COMMISSION.

PROGRAM OF THE EIGHTH MEETING, CHICAGO,

DECEMBER 17, 1910.

12 noon. Informal luncheon, Drexel Café, 39th St. and Cottage Grove Avenue.

1.30 P.M. Meeting at the Pumping Station, Sanitary District of Chicago, 39th St. and Lake Michigan.

"Sanitary Conditions of the Calumet River in Indiana," J. H. Brewster, chemist, Indiana State Board of Health.

"Disposal of Starch Factory Wastes," T. B. Wagner and O. H. Sjostrom, Corn Products Refining Co., Chicago.

"Sewage Experiment Station, Sanitary District of Chicago," Langdon Pearse and Dr. Arthur Lederer, Sanitary District of Chicago.

W. A. EVANS, M.D., *President*,
EDWARD BARTOW, *Secretary*.

NATIONAL COMMERCIAL GAS ASSOCIATION.

SIXTH ANNUAL CONVENTION, BOSTON, DECEMBER 6-9, 1910.

The National Commercial Gas Association convened in Boston, Mass., on the above-mentioned dates and carried out a long and interesting program. A prominent feature of the convention was an exhibition of gas appliances and apparatus of all types which was open to the general public from December 7-13. A most interesting part of the exhibit was a complete operating plant showing the manufacture of incandescent gas mantles. The process was carried out from the knitting of the fabric to the packing of the final product and occupied the entire stage of the Mechanics Hall where the convention was held. The exhibition was made by the Welsbach Company and proved of the greatest interest both to the gas men and members in attendance at the convention and the public.

AMERICAN CHEMICAL SOCIETY.

METHODS OF ANALYSIS AND TESTS OF FATS AND OILS SUGGESTED BY THE SPECIAL COMMITTEE OF COMMITTEE ON THE UNIFORMITY OF ANALYSIS OF FATS AND FATTY OILS.

(These methods are proposed tentatively with the object of inviting criticism and discussion.)

1. MOISTURE AND VOLATILE MATTER.

Weighing Out Sample.—By the application of gentle heat soften, but do not melt, the sample, and emulsify thoroughly by means of a mechanical egg beater (or other suitable device). Of the thoroughly emulsified sample weigh out for the standard methods from 5 to 20 grams according to the method used from weighing bottle into a watch glass or shallow glass dish whose sides are not more than 1 cm. high.

Standard Method No. 1, Moisture and Volatile Matter at 110° C.—A 5-10 gram sample weighed out as above is heated in an oven held at a constant temperature of 110° C. until constant weight is attained. Constant weight is attained when successive weighings thirty minutes apart show a loss of not more than 0.05 per cent.

Standard Method No. 2, Moisture and Volatile Matter.—A 5-10 gram sample weighed out as above is heated in a vacuum oven held at 50° C. under a pressure of not more than 30 mm. of mercury for four hours. (The tension of water vapor at 50° C. is 92 mm.)

Routine Method, Moisture and Volatile Matter.—The sample weighed out in a glass or aluminum beaker as above is heated on a heavy asbestos board over burner or hot plate, the sample at no time being allowed to reach a temperature greater than 130° C. During the heating the beaker is rotated gently on the board by hand to avoid sputtering or too rapid evolution of moisture. The proper length of time of heating is judged by absence of condensation on a cold watch glass held over the beaker, by the absence of rising bubbles of steam, by the absence of foam or by other signs known to the operator. Cool in desiccator and weigh. Report loss as moisture.

2. MOISTURE.

The term "moisture," as here used, refers to the chemical substance "water" physically incorporated in the fats and fatty oils.

Standard Method.—(Similar to that mentioned by Ubbelohde.)

100 grams of the sample are mixed with 100 cc. of xylene in a suitable distilling flask, and about 50 cc. slowly distilled off over a free flame. The distillate containing the water is collected in a tube 0.75 cm. diameter graduated in 1/10 cc., and the percentage of water read off directly from the volume of

water contained in the tube. Correction is to be made for the solubility of water in xylene. Details to be supplied.

Note: The boiling point of xylene is 138°C .

3. SUSPENDED IMPURITIES.

Definition—Suspended impurities in fats and fatty oils are those non-fatty solid substances physically incorporated therewith and insoluble in hot petroleum ether, such as particles of wood, coal, fibers, and mineral matter. They are determined by the standard method given below.

Determination: Standard Method.—A sufficiently large sample to be representative should be weighed out and dried, or the residue from a moisture and volatile matter determination may be used. Usually from 5–20 grams should be used. The sample is dried in a beaker over asbestos board, keeping the beaker in motion by hand to prevent sputtering. The sample is then dissolved in hot petroleum ether (B. P. $50\text{--}70^{\circ}\text{C}$.) by gentle boiling on a water bath, filtered on a Gooch crucible or porous crucible, washed thoroughly with a boiling petroleum ether (B. P. $50\text{--}70^{\circ}\text{C}$.), dried to constant weight and weighed.

4. FREE FATTY ACIDS.

Preparing Neutral Alcohol.—Take commercial 95 per cent. alcohol, add 50 grams powdered caustic soda per liter, boil with reflux condenser for a period of six hours, allow to stand for twenty-four hours, and then distil. Alternate method.

Determination.—From 5–15 grams of the sample are weighed into an Erlenmeyer flask (100 cc. capacity) and melted on the steam bath, if solid at ordinary room temperature. Add 100 cc. of hot neutral alcohol. Titrate with $\text{N}/2$, $\text{N}/4$ or $\text{N}/10$ sodium hydrate, using phenolphthalein as indicator. Where the fat is known to have a mean molecular weight of 282 or thereabouts, that figure is to be used in calculating the percentage of free fatty acids. Report also the acid number: milligrams KOH required to neutralize 1 gram. The percentage of free fatty acids is to be calculated on the basis of sample freed from moisture and volatile matter.

5. TITER.

Bureau of Chemistry, Bulletin 107, Revised.

Method Proposed by L. M. Tolman as Follows.—"Weigh 75 grams of fat into a metal dish, and saponify by using 60 cc. of 30 per cent. sodium hydrate (36° Beaumé caustic soda) and 75 cc. of 95 per cent. by volume alcohol, or 120 cc. of water. Boil down to dryness, with constant stirring, to prevent scorching. This should be done over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid (25° Beaumé sulphuric acid) to free the fatty acids, and boil until they form a clear transparent layer. Collect the fatty acids in a small beaker and place on the steam bath until the water has settled, then decant them into a dry beaker, filter, using a hot-water funnel, and dry twenty minutes at 100°C . When dried, cool the fatty acids to 15° or 20°C . above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 by four inches) and made of glass about 1 mm. in thickness. This is placed in a sixteen ounce, salt-mouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high ($2\frac{4}{5} \times 6$ inches), fitted with a cork which is perforated so as to hold the tube rigidly when in position. The thermometer, graduated to 0.1°C ., is suspended so that it can be used as a stirrer, and the mass is stirred slowly until the mercury remains stationary for thirty seconds. The thermometer is then allowed to hang quietly with the bulb in the center of the mass, and the rise of the mercury observed. The highest point to which it rises is taken as the titer of the fatty acids

"The fatty acids are tested for complete saponification as follows: Three cc. of the fatty acids are placed in a test tube and 15 cc. of alcohol (95 per cent. by volume) added. The mixture is brought to a boil and an equal volume of ammonia (0.96 sp. gr.) added. A clear solution should result, turbidity indicating unsaponified fat. The room temperature must be reported"

Proposed Exceptions—The fat is to be saponified in an iron or porcelain dish, and fatty acids set free in porcelain, fatty acids to be dried twenty minutes at 105°C . instead of at 100°C .

6. UNSAPONIFIABLE MATTER

Definition.—The non-fatty acid constituents of fats and fatty oils, soluble in petroleum ether (B. P. $35\text{--}50^{\circ}\text{C}$.).

DETERMINATION.

Standard Wet Method.—Three grams of the sample, free from moisture and volatile matter, are weighed into a 150 cc. flask, and a 30 per cent. excess of strong, colorless or nearly colorless alcoholic potash solution added. The contents are boiled for one hour under a reflux condenser, and then transferred to a stoppered 100 or 150 cc. cylinder and made up to 50 cc. with cold water. Add 30 cc. of redistilled petroleum ether (boiling point $35\text{--}50^{\circ}\text{C}$.) and agitate vigorously. Draw off the petroleum ether layer by means of slender glass siphon. Repeat this operation with five separate portions of petroleum ether. Place the 150 cc. of petroleum ether into a Squibb's pear-shaped separatory funnel (250 cc.) and wash three times with 20 cc. of 50 per cent. alcohol. Pour the contents of the funnel into a tared flask and distil off the greater part of the petroleum ether and complete the drying on a steam bath and in an oven, the latter held below 105°C .

Standard Dry Method.—Approximately 5 grams of fat or oil are weighed into a 200 cc. capacity Soxhlet or Erlenmeyer flask, and saponified with sufficient alcoholic sodium hydrate solution to give 50 per cent. excess of sodium hydrate by boiling under a reflux condenser for $\frac{1}{2}$ hour to one hour or until saponification is complete. The solution is then transferred to a four-inch porcelain evaporating dish (the flask being rinsed with hot alcohol) and dried on a water bath. The drying is completed in the oven at 120°C . for one to two hours. Grind the dried soap in an agate mortar with 10–15 grams granular, anhydrous sodium carbonate and place the whole in a 33×80 mm. S. & S. extraction thimble, using a fat-free plug of cotton to cover the charge. Place the thimble and contents in oven and redry for one hour at $110\text{--}120^{\circ}\text{C}$. The extraction is made with redistilled light petroleum ether boiling from $35\text{--}50^{\circ}\text{C}$. During the extraction if a Soxhlet or Knorr apparatus is used the open end of condenser must be protected against atmospheric moisture by a CaCl_2 tube. All connections of the apparatus must be tight. The extraction is allowed to proceed for about ten hours (if a Soxhlet apparatus is used at least 50 discharges). Transfer the extract to a weighed beaker, evaporate solvent on the water bath and dry in an oven to constant weight. Test the extract by redissolving in light petroleum ether: a clear solution should be obtained if the determination has been properly carried out.

7. METALLIC SOAPS.

Definition.—The insoluble metallic soaps in the present sense are the fatty acid compounds of bases other than the alkalies. They are insoluble in water.

DETERMINATION.

Standard Method No. 1.—The filtrate from the suspended impurities determination (including the hot petroleum ether washings) is evaporated to a bulk of about 200 cc., and allowed to stand over night or 12 hours in a cool place ($18\text{--}20^{\circ}\text{C}$.). It is then filtered from the separated insoluble metallic soaps on a Gooch crucible, washed with cold petroleum ether (B. P. $35\text{--}50^{\circ}\text{C}$.), dried and weighed.

Standard Method No. 2.—The filtrate from the suspended impurities determination is evaporated, burned and ignited to constant weight. (a) The weight of the ash from metallic soaps thus obtained is to be reported as such. (b) Considering the ash to consist entirely of calcium oxide, it is to be calculated to normal soap, using 281 as molecular weight of fatty acid and reported as lime soap.

PROPOSED DISCUSSION OF METHODS.

Correspondence in regard to the above methods should be addressed to W. D. Richardson, 4215 Prairie Ave., Chicago, Ill.

PERSONAL NOTES.

On November 9, 1910, the City of Philadelphia, on the recommendation of the Franklin Institute, awarded the John Scott Legacy Premium and Medal to Dr. L. H. Baekeland, of Yonkers, New York, for his invention of Bakelite, in accordance with the report of the Institution's Committee on Science and Arts, adopted May 4, 1910.

Seven eminent scientists and technologists have been honored by the Franklin Institute of Philadelphia in being awarded Elliott Cresson medals for "distinguished, leading and directive work" in their respective fields of endeavor. The medals are the highest awards in the gift of the institution. The recipients are:

Dr. Harvey W. Wiley, chief chemist to the department of agriculture, Washington, for his work in agricultural and physiological chemistry.

John Fritz, Bethlehem, Pa., for his work in the development of the iron and steel industries.

John A. Brashear, Pittsburg, Pa., for his work in the production and perfection of instruments for astronomical research.

Edward Weston, Newark, N. J., for his work in electrical discovery and in the advancement of electrical application.

Ernest Rutherford, professor of physics, Owens College, Victoria University, Manchester, England, for his work in the advancement of the knowledge of electrical theory.

Sir Joseph John Thomson, Cavendish professor of experimental physics, Cambridge University, England, for his work in the advancement of knowledge of the physical sciences.

Sir Robert A. Hadfield, Sheffield, England, for his work in the advancement of knowledge of metallurgical science.

Elliott Cresson medals have been awarded by the Franklin Institute at infrequent intervals during the last sixty or seventy years.

RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., N. W., Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department. ¶

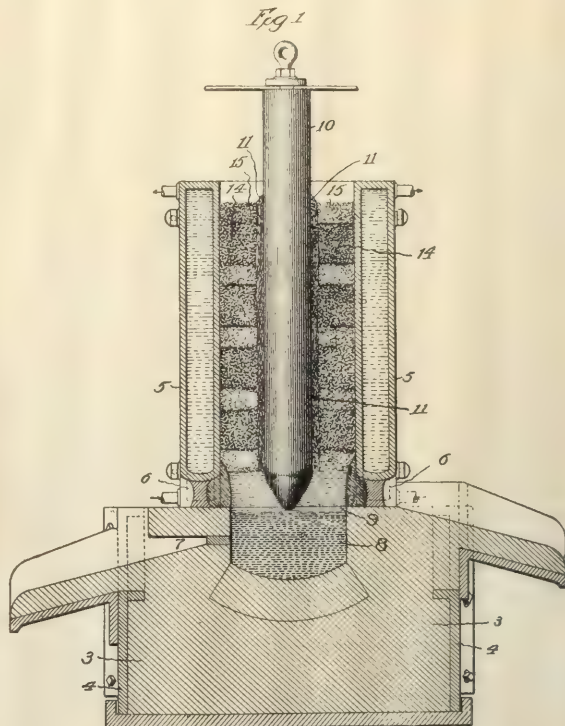
Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

974,608. Process of Smelting Ore. FREDERICK T. SNYDER, Oak Park, Illinois. Patented November 1, 1910.

This invention relates to a process of smelting ore, with especial reference to the treatment of iron ore, for the direct production of steel therefrom.

Previous attempts to produce steel directly from iron ore by electric smelting have met with practical difficulties, one of which has been the rapid destruction of the furnace walls by corrosive slags. Attempts to overcome this by making the crucible of carbon result in impairing the product because the carbon combines with the molten metal and produces pig iron instead of steel.

In accordance with this invention, only sufficient carbon is mixed with the furnace charge to secure reduction of the metal from the ore and to produce steel; and the molten metal when produced is collected in a crucible of refractory, and preferably basic, material, such as dolomite, while the slag is confined by a fluid, cooled wall in contact therewith, which freezes the outlying portions of the slag bath to form a lining or container composed of solid slag. The necessary heat is produced by passing



an electric current between carbon electrodes which dip into the molten slag from the top, but do not extend downward deep enough to reach and contaminate the steel in the crucible. Two or more electrodes are provided, for taking the current both into and out of the furnace through the top, in order to avoid having any carbon in the crucible or as a part thereof.

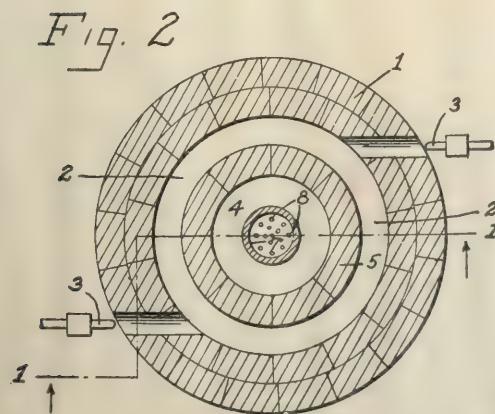
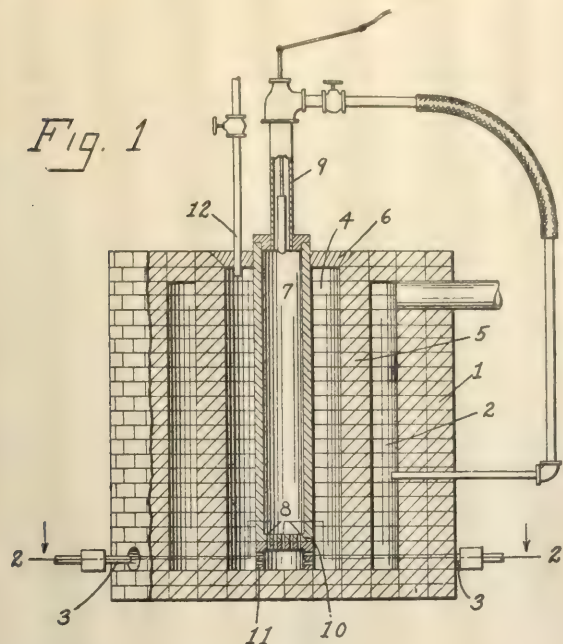
The water-jackets protect the masonry crucible on which they rest to a depth of several inches, and the metal level in the crucible is kept high enough so that the slag cannot reach a low enough level to cut through the crucible under the water-jackets. The metal, however, is not allowed to accumulate in the crucible to such an extent that it would come into contact with the water-jackets, as this would freeze the metal solidly upon the jackets, and result in a very great heat-loss. This loss is prevented, and the steel kept from contamination by keeping it in the refractory crucible, the material of which also serves to actually purify the steel by taking up small amounts of phosphorus and sulfur therefrom.

975,076. Process of Carbonizing. ALBERT F. ROCKWELL, Bristol, Conn. Patented November 8, 1910.

In carrying out this invention a carbon-bearing gas is first brought to a heat as great as that of the material being treated and is at such temperature then introduced into contact with the said material. In this way the incoming gas does not interfere with the carbonizing operation by chilling the material. Indeed, at the beginning of the operation, the gas is generally at a temperature greater than that of the said material, in which event said incoming gas not only does not chill the material but assists in heating the same.

The patentee employs a heating chamber separate from the

flask which contains the material to be treated but communicating with said flask, such heating chamber being of a temperature at least equal to (and sometimes greater than) that of the flask, and to introduce a carbon-bearing liquid, such as hydro-



carbon oil, into said heating chamber in small quantities, whereby said oil is converted into gas and heated, the heated gas then passing into said flask. The gas thus creates its own pressure in the heating chamber whereby said gas is forced into said flask and into intimate contact with the material therein.

Preferably the air is driven away from the material before the latter reaches the degree of heat which would produce oxidation, and air is kept away from said material until the carbonizing process is completed, thus avoiding oxidation and its attendant disadvantages. This expulsion of the air is accomplished by permitting a small amount of carbon-bearing gas to enter the flask containing the material before the latter has become sufficiently heated to oxidize, such supply of gas being sufficient to drive off the air, but insufficient, when initially supplied, to produce appreciable carbonization. After the air is thus driven off, the supply of gas is cut off and the gas in the flask lies dormant, thus excluding the air, until the material has been brought to the desired temperature for carbonization when the gas is admitted in carbonizing quantity and the process of carbonizing commences.

In practicing the process, the material is placed in the flask,

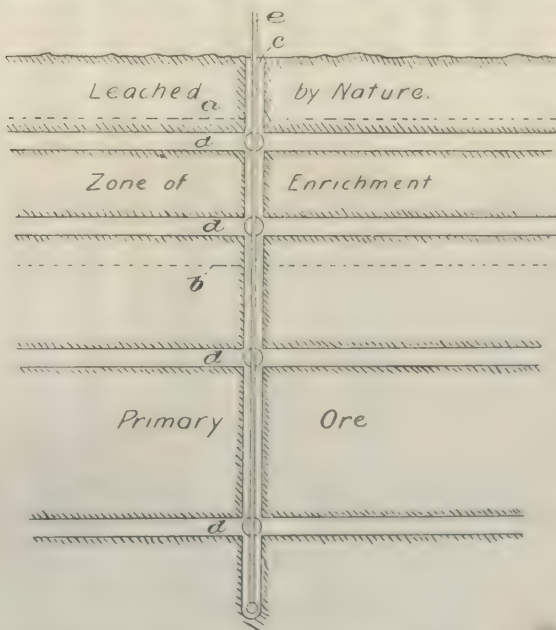
the removable cover put in place to close the heating chamber and the furnace heated. Preferably, a small amount of the hydrocarbon oil is now introduced into the heating chamber 4, the resulting gas flowing into the flask 7 and driving off the air therein to prevent oxidation as above explained. When the proper temperature has been attained, say a red heat, oil is again admitted through the inlet 12, and such oil is at once converted into gas and heat to the temperature of the heating chamber, which is always as great as the temperature of the material in the flask. The heated gas, of course, creates its own pressure in the heating chamber and is thus forced through the inlets 8 into the flask and into intimate contact with the material therein, such heated gas not chilling the material as it enters the flask. Indeed, at the beginning of the operation the temperature of the gas is greater than that of the material in the flask, so that at the outset the incoming gas not only does not chill the material but such gas assists in heating the same.

When it is desired to distribute the carbon throughout the body of the article as above described, the supply of oil from the inlet 12 is merely cut off, the flask being continued at carbonizing temperature until the desired distribution of carbon is effected.

975,106. Process of Extracting Copper from Ore. WILLIAM L. AUSTIN, of Riverside, Calif. Patented Nov. 8, 1910.

This invention relates to a process of extracting copper which is especially applicable in localities where there are minerals which can be rendered soluble, such, for example, as copper minerals, distributed through more or less porous rock.

Such rock as porous porphyry (granite-porphry) for example, may contain, in the aggregate, a quantity of valuable mineral although too small a percentage to be worked profitably by ordinary mining operations. The mineral may, however, be profitably extracted by the process which I have discovered, which consists in applying a solvent so as to percolate through the mineral-bearing material without removing it by the usual mechanical mining operations from its original location, the percolating liquid extracting the mineral by leaching, and in providing for the collection and subsequent removal of the re-



sulting solutions, from which the metals may then be separated in any suitable or usual manner.

In carrying out the process, an artificial drainage level is created at a point or points below the surface of the rock through

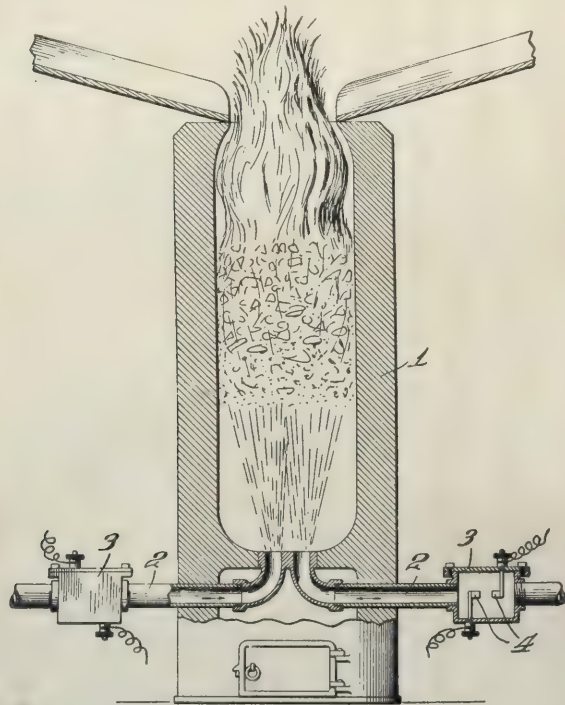
which the copper minerals are distributed. This may be accomplished by running levels and cross-cuts at different horizons, and by sinking shafts to a suitable depth, and in so locating these workings that water or any liquid permeating the rock will seek the lower levels and be collected therein. If, therefore, a quantity of water is distributed over the surface of the rock, or through any of the upper levels, it will percolate through the same leaching out the copper minerals and collecting in the lower workings. The resulting liquids are then removed, as by a pump, for further treatment to extract their metallic contents. It is desirable to carry out the process of extracting the metals from the solutions at or near the location of the ore-body so that the liquids from which the metals have been separated may, if desirable, be again allowed to pass through the rock. It is, however, immaterial, how the water is supplied, it being frequently practicable to divert the water from a running stream, or any reservoir, and to distribute it throughout the upper parts of the ore-body.

975,625. Process of Extracting Iron from its Ores. STEPHEN G. MARTIN, of Chicago, Illinois. Patented Nov. 15, 1910.

This invention relates to a process of extracting iron from its ores and its subsequent conversion into steel, and said process being applicable to the so-called non-Bessemer as well as to Bessemer ores, and by my improved process either one of said ores can be readily converted into iron of such quality as to be immediately available for the Bessemer blow.

The desirable qualities in iron applicable for the manufacture of steel are those of a metal free, or practically free, from sulfur, silicon, phosphorus and the like, and it is well known that such metalloids remain in undesirable quantities in iron produced by ordinary processes in blast furnaces.

The invention consists in dispensing with the use of atmospheric air in the blast furnace and substituting therefor modified or ionized air made by passing atmospheric air through the flame of an electric discharge, and this modified or ionized air passes



into the blast furnace in an absolutely dry state, and in such condition attacks the furnace charge with a high degree of chemical energy, which reduces the charge in much less time than is now required by methods in general use while the re-

sultant metal is found to be homogeneous iron practically free from all metalloidal impurities and of the quality and conditions most desirable in iron which is to be converted into steel by the Bessemer process.

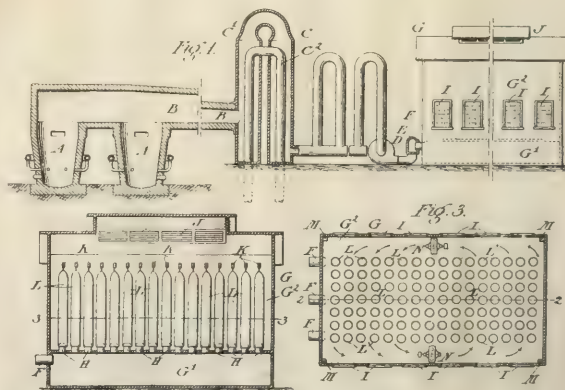
It has been demonstrated that when ordinary atmospheric air is passed through the flame of an electric discharge or through a flaming arc of electricity, a gaseous medium is produced consisting of pure air and gaseous peroxid of nitrogen, and this is the sense in which the applicant uses the expression "modified or ionized air," the gaseous peroxid of nitrogen being the active agent in the process. This gas is conducted into the furnace as rapidly as it is formed. Under these conditions dissociation of the gas (the temperature of the furnace being taken into consideration) does not take place during its passage from its source of supply to the furnace. It is, therefore, not necessary that means be provided to insure stability of the gas.

975,768. Apparatus for Manufacturing Sublimed White Lead.

LOUIS S. HUGHES, of Joplin, Missouri. Patented Nov. 15, 1910.

This invention relates to apparatus for the manufacture of lead sulfate pigment and particularly to the construction of the screen or bag house used in separating the pigment from the gases from the furnaces wherein the sulfate is produced.

The lead sulfate pigment known in the market as "sublimed white lead" is made by treating lead-bearing material in oxidizing furnaces adapted to convert the lead in large part into a finely divided "fume" of lead sulfate, and the gases and fume



issuing from the furnace after being subject to various treatments to eliminate heavy and discoloring impurities are passed through cooling flues to reduce their temperature and then carried to the bag house where the pigment is separated from the gases.

The lead sulfate pigment as heretofore made has been found liable to harm when mixed with oil, and after many tests and experiments it has been ascertained that this tendency is due to the occlusion in the pigment of acid compounds of sulfur either SO_2 or H_2SO_3 .

The patentee claims to have discovered that the presence of the injurious acid in the pigment can be avoided by maintaining the gas and fume up to and during the screening operation at temperatures so high that the acid is maintained in dry vaporous form and thus prevented from becoming occluded in the pigment since it passes freely through the screen bags with the gases.

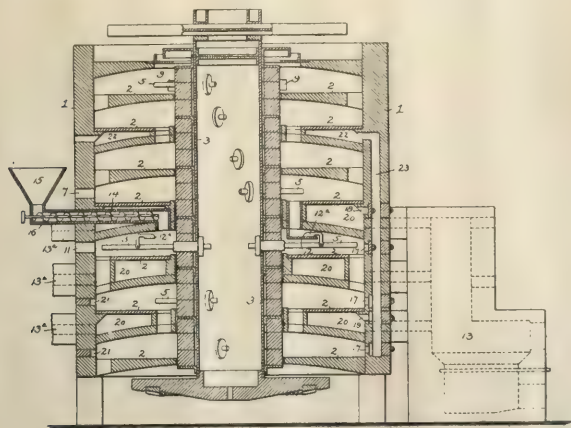
As heretofore constructed and used the screen chamber or bag house used in the separation of the furnace gases from the pigment has been quite freely ventilated, it being considered and used as, in effect, a part of the gas-cooling system, and free ventilation being also desired to get rid of poisonous gases in the bag house, and thus make it possible for attendants to enter it.

The invention consists in using in connection with the producing furnaces and cooling flues a bag house constructed with closed walls and opening only at its top so that the bag house will constitute in effect a part of the flue system of the furnace in which the fabric bags are already surrounded and submerged by an atmosphere of furnace gas maintained at a constant and, as compared with former practice, a high temperature. The temperature must not exceed 350° F. in view of the danger of burning or charring the bags, and it must not be less than 250° F. to secure the elimination of the acid compounds of sulfur.

976,525. Treating Sulfids or Sulfates. UTLEY WEDGE, of Ardmore, Penna. Patented Nov. 22, 1910.

The object of this invention is to facilitate the elimination of sulfur in roasting sulfids or sulfates, such as those of zinc or nickel.

In the roasting of sulfids or ores containing the same, the elimination of the sulfur remaining after the sulfid has passed through the preliminary stages of the roasting process requires the employment of an objectionably high temperature and even in such case the sulfur is not completely eliminated and objectionable amounts of sulfur are likely to be left in the



calcined or roasted material, owing to the formation of basic sulfates which are difficult to roast. In order to overcome this difficulty the patentee combines with the material, after it has passed through the first stages of its treatment, in the roasting furnaces, a reagent which will reduce the basic sulfates, the elimination of the remaining sulfur content down to the point desired being then readily effected without the employment of an objectionably high temperature during the latter part of the treatment.

The accompanying illustration shows the apparatus employed in the practice of patentee's process.

INDUSTRIAL AND TRADE NOTES.

GERMAN POTASH CONTRACTS.

Robert S. Bradley, of Boston, who is chairman of the board of directors of the American Agricultural Chemical Co., has issued the following statement in regard to the German potash situation, which recently assumed such an acute phase as to necessitate the sending of a special investigator over there.

"The potash business has been controlled by a German syndicate for more than 30 years. This control has been exercised not only over the production of the commodity, but its sale in all the markets of the world. It has been the custom to form such a syndicate for a period of five years, and the

last syndicate expired by limitation at midnight of June 30, 1909.

"For months before attempts had been made to form a new syndicate. I had been in Berlin for some time investigating and preparing to buy potash in case an opportunity was offered. By midnight of the day mentioned the delegates representing about 60 mines, who had been in session, had failed to come to an agreement. This caused an open market at the moment and I immediately made contracts running two years, together with option to run one year on a future contract period of five years. This covered the entire requirements of the American Agricultural Co. for seven years.

"At half past 1 o'clock that same morning, the president issued an edict calling a meeting of the delegates for 9 o'clock when a new syndicate was formed. This, of course, closed the opportunity to buy potash at less than syndicate prices.

"The contracts I had made were reported, of course, to the new syndicate and the news caused some consternation among the delegates because the prices were about 35 per cent. below the prices that had been ruling. For example, the syndicate price of muriate of potash landed in New York was \$33 a ton, while according to my contract it would be about \$20.

"In August they sent representatives over here to negotiate for a compromise of my contracts, but without result. The next month delegates representing about 60 American manufacturers went to Berlin and obtained a duplication of my contracts in consequence of their holding contracts made with one of the Schmittmann mines, whereby the latter guaranteed to these American manufacturers the same prices that my company might obtain. Schmittmann was therefore legally bound to give these manufacturers the same terms I had obtained, so that now instead of a matter of \$6,000,000 being involved there was \$25,000,000.

"Geheimrath Kempner and Herr Bielman, another director of the potash syndicate, came over here the following December. We volunteered to meet them half way and divide the difference between the syndicate prices and the contract prices, because they presented a draft of an Imperial potash law which had been into the Bundesrath. This bill imposed an export duty on potash that would countervail the prices mentioned in our contracts.

"They accepted our offer on principle, but in figuring out the prices, they raised them sufficiently to countervail all the advantages left on a half-way compromise basis. We then broke off negotiations. Secretary Knox made a strong, emphatic protest to the Imperial German Government through Ambassador Hill, and the potash bill was subsequently withdrawn.

"Immediately thereafter, the United States and Germany completed a commercial treaty which gave Germany the benefit of the American minimum tariff. In May following, the Reichstag passed a potash law more drastic and more damaging in its effects on American contracts than the original Bundesrath bill which had been withdrawn at the protest of this government. But, at the same time, Ambassador Hill received assurance from the German foreign office that the law, as finally amended, would not invalidate, impair or affect the American contracts.

"Notwithstanding this assurance all shipments of potash, after the law went into effect, were taxed \$22 a ton over the contract price. This made the price of muriate of potash \$42 a ton, instead of \$20. The law imposes a duty in the form of a penalty tax for production over the allotted quota of a mine, and as the two mines which hold the American contracts are the only ones which overproduce, the tax affects only American contracts, and this is therefore absolutely discriminatory against American citizens.

"Negotiations were opened in Berlin. The American committee for the second time made a voluntary proposal to the Germans to divide the difference and meet them half way,

thus giving up over \$12,000,000. The Germans flatly refused to consider the proposal. Therefore the American committee left Berlin."

DISCOVERY OF "SHEELITE" IN NOVA SCOTIA.

(From Consul John E. Kehl, Sydney.)

An interesting event in the mineral development of the Province is the recent discovery of "sheelite" in Halifax County, Nova Scotia.

Sheelite is one of the minerals containing tungsten. It is of no known use in itself, excepting as an ore from which tungsten may be extracted. The mineral is chemically a tungstate of calcium. As an ingredient in the chemical side of steel-making it is quite important. At present the world's annual output, coming mostly from Sweden, is placed at 4,000 tons. If present indications are correct, the recent discovery in Nova Scotia will not only yield sufficient for the steel plants in the Province, but will have an effect on the markets of the world. The ore is reported to yield 60 per cent. of tungsten acid to the ton of sheelite. At present 25 men are at work on the preliminary experiments. It is believed that Mr. Hiram Donkin, deputy commissioner of mines, Halifax, Nova Scotia, will give interested parties all reasonable information.

IRON AND STEEL BY ELECTRIC PROCESS.

(From Consul-General Henry Bordewich, Christiania, Norway.)

Experiments to produce iron and steel from Norwegian ores by the electric process have been made during the last three or four years, partly by aid from the Government, in response to a petition sent to the Department of Commerce and Industries by the Christiania Polytechnical Society. Private interest has in this manner been awakened, and the industry now promises to become one of considerable importance. The Norwegian iron ore is often so poor that smelting by the old process was found profitless.

The owners of a paper mill at Tinfos, in Notodden, Telemarken, Norway, have for some time been making experiments for the purpose of producing iron by melting iron ore by the use of electricity as the source of heat. The works were completed in February last, and there has already been an output of 250 tons of iron. The ore used has been mined partly at Lango, near Kragerø, and partly at Klodeberg, near Arendal. The melting was accomplished by the use of an electric furnace of about 500 horse-power. This is the first iron produced by the new process, and in commemoration of the event there has been cast and sent to the Christiania University an ingot of the metal weighing 60 kilos and provided with an appropriate inscription.

A stock company, styled the Hardanger Electric Iron and Steel Works, is at present being organized. The capital stock is to be \$294,800, of which there has already been sold \$160,800. There are 4,400 shares of \$67 each. The works are to be located at Ullensvang, in Hardanger, on the west coast, and the object is to produce iron and steel from Norwegian ores by a patented electric process of Swedish origin. The company has secured electric energy from the adjoining water power at Tysse, for a period of thirty years, at a cost of \$8.04 per horse-power; 4,200 horse-power will be required. The ore to be used is to be bought from mines in other districts on the best obtainable terms. The transportation of the ore will be found expensive, but it is believed that this drawback will be offset by the cheap power and excellent harbor facilities at the place.

Among the principal promoters of the undertaking is the stock company styled Det Norske Aktieselskab for Elektrokemisk Industri. The director of this company is interested in the Tysse water powers, which are to furnish energy for the smelting works. Among the promoters are many influential and responsible men, and it is believed that the required capital will be raised without difficulty.

MINERAL PAINT PRODUCTION.

(From advance chapter on Mineral Resources by the U. S. Geological Survey.)

The annual consumption of paints and varnishes in the United States exceeds in value \$200,000,000; the railways alone will distribute among the paint and varnish manufacturers in 1910 between \$20,000,000 and \$30,000,000. It is, therefore, a matter of great interest to comprehend the various products which help to make up this vast trade.

The production of the natural mineral pigments and metallic paints and mortar colors in the United States in 1908 and 1909, together with the imports of similar products during the same years, all quantities being given in short tons, was as follows:

Description.	Quantity.		Value.	
	1908.	1909.	1908.	1909.
	Tons.	Tons.		
Ocher.....	17,019	14,310	\$156,360	\$137,880
Umber and sienna.....	2,756	1,546	70,996	43,872
Metallic paint.....	16,224	25,414	182,007	256,373
Mortar colors.....	9,026	11,620	86,961	116,126
Slate and shale ground.....	4,828	8,247	40,220	58,882
Total.....	49,853	61,137	536,544	613,133

Metallic paint and mortar colors are red and brown iron oxides, produced either by grinding the mineral found in the natural state or by roasting iron carbonate. Slate and shale were ground for pigments, principally in Pennsylvania and New Jersey.

The imports of ocher, umber, and sienna, crude, dry, and ground in oil were as follows:

Item.	Quantity.		Value.	
	1908.	1909.	1908.	1909.
	Tons.	Tons.		
Ocher.....	4,127	6,848	\$ 75,076	\$110,664
Umber.....	1,204	1,596	20,264	26,381
Sienna.....	887	1,205	28,865	33,334
Total.....	6,218	9,649	124,205	170,379

The following statement shows the world's production of ocher:

Country.	Quantity.		Value.	
	1907.	1908.	1907.	1908.
	Tons.	Tons.		
United States.....	16,971	17,019	\$164,742	\$156,360
United Kingdom.....	16,455	70,117
France.....	36,217	36,442	423,830	457,072
Germany.....	1,679	5,290
Canada.....	5,828	4,746	35,569	30,440
Belgium.....	220	876
Japan.....	331	2,531
Cyprus (4 ports).....	7,301	20,279
Total.....	85,002	723,234

Pigments Made Directly from Ores.—The important pigments made directly from ores of valuable metals are zinc oxide, lead zinc oxide, zinc lead, sublimed white lead, and sublimed blue lead. The quantities and value produced in the United States were as follows:

Description.	Quantity.		Value.	
	1908.	1909.	1908.	1909.
	Tons.	Tons.		
Production:				
Zinc oxide.....	56,292	68,974	\$5,072,460	\$6,156,755
Zinc lead.....	8,430	7,655	778,200	634,714
Sublimed white lead.....	9,100	9,915	973,700	1,070,820
Sublimed blue lead.....	1,311	981	121,923	101,043
Total.....	75,133	87,525	6,946,283	7,963,332
Imports of zinc oxide:				
Dry.....	2,318	3,059	262,876	342,999
In oil.....	105	268	16,798	54,085
Total.....	2,423	3,327	279,674	397,084

Chemically Manufactured Pigments.—Under this heading are grouped the important lead pigments made from pig lead and lead compounds, and such minor pigments as lithopone and Venetian red, both of which are chemically precipitated from mineral salts. Much of the material now sold as Venetian red, however, instead of being precipitated from ferrous sulphate and calcium hydroxide, is made in several ways, such as by calcinating both pyrites and a mixture of ferrous sulphate and terra alba, and also by grinding natural red iron oxide with a white base, such as ground oyster shells.

The following statement shows the amounts and value of the chemically manufactured pigments produced in the United States in 1908 and 1909, together with the quantities and value of similar pigments imported during the same years:

Description. Production.	Quantity.		Value.	
	1908. Tons.	1909. Tons.	1908.	1909.
Basic carbonate white lead:				
In oil.....	101,109	115,259	\$12,552,771	\$14,736,360
Dry.....	31,479	32,840	3,338,830	3,468,722
Red lead.....	16,720	19,103	2,065,202	2,335,799
Litharge.....	15,542	20,690	1,887,506	2,363,002
Orange mineral....	397	590	65,498	98,723
Lithopone.....	8,292	14,847	639,483	1,105,281
Venetian red.....	8,825	8,358	159,650	145,733
Total.....	182,364	211,687	20,708,940	24,253,620
Imports.				
Corroded white lead.	270	347	30,452	39,963
Red lead.....	323	380	28,155	30,428
Litharge.....	48	45	3,327	3,740
Orange mineral....	243	248	26,645	27,562
Venetian red.....	1,557	2,000	25,745	28,864
Total.....	2,441	3,020	114,324	130,557

Consumption of Paints and Varnishes.—G. B. Heckel, secretary of the Paint Manufacturers' Association of the United States, is quoted as follows:

The annual consumption of paints and varnishes in the United States exceeds \$200,000,000, white lead, zinc oxide, and linseed oil alone amounting to nearly \$40,000,000. Roughly speaking, this consumption is about equally divided between house-painting products and technical products (railway and bridge paints, wagon and implement paints, etc.). During the two years of depression paint consumption in the first classification was reduced by about one-half, this reduction being about balanced by the remaining demand in the second classification.

The consumption of paint by the railways of the country has been conservatively estimated at from \$12,000,000–15,000,000. But it must be remembered that, during the past two years, this consumption has been limited on the basis of "rigid economy" and that now not only must the railways add their normal annual equipment, but they must also add the new equipment deferred for two years, besides providing for the repairs and renewals deferred during the same period; we shall, therefore, be conservative in estimating that the railways during the coming year will be forced to distribute between \$20,000,000 and \$30,000,000 among paint and varnish manufacturers.

EXPORT PRICES OF GERMAN POTASH.

(From Consul-General Robert P. Skinner, Hamburg.)

The manufacturers of nitrate of potash in Germany have formed a trust agreement under which identical prices are demanded at the several factories. It is only possible at times for individual dealers to propose better terms than can be obtained direct, because such dealers make contracts for 50 or 100 tons at a time, and are thereby enabled to break large lots into small ones, and sell the smaller quantities below the trust quotations.

The best prices within my possession on powdered and granulated nitrate of potash for export to Africa, Asia, North America,

Australia, Spain, Portugal, and Greece follow: In quantities less than 5,000 kilos (5 metric tons), 42 marks (\$9.996) per 100 kilos (220 pounds); at least 5,000 kilos, 41 marks (\$9.758) per 100 kilos; at least 50,000 kilos (50 tons), 40 marks (\$9.52) per 100 kilos. Small, medium, and large crystals cost 1 mark (\$0.238) per 100 kilos more. Long crystals (strahlen) cost 2 marks (\$0.476) per 100 kilos more.

These prices are f. o. b., packed in barrels of 400 to 500 kilos (880 to 1,100 pounds). For smaller barrels an extra charge will be made as follows: Barrels of 550 to 660 pounds, 9.52 cents; 440 pounds, 14.28 cents; 330 pounds, 19.04 cents; 220 pounds, 23.8 cents; 110 pounds, 47.6 cents; double bags of 220 pounds, 2.38 cents; 110 pounds, 1.19 cents.

The prices quoted are f. o. b. Hamburg. Freight from Hamburg to New York is quoted at the rate of 15s. per ton of 1,000 kilos (\$3.65 per 2,204 pounds), or 13s. 6d. (\$3.28) on annual contracts.

OUTLOOK OF CHILEAN NITRATE BUSINESS.

(From Consul Alfred A. Winslow, Valparaiso.)

The nitrate industry of Chile has made good progress during the past year, notwithstanding the low prices prevailing for nitrate in the markets of the world.

A number of new nitrate works have been opened, and most of the well-equipped plants have been running at full capacity, and seemingly at a good profit. During the first nine months of 1910 there were 3,942,648 tons of nitrate produced in Chile, against 3,200,039 tons for a like period in 1909, and 3,092,506 tons exported against 2,847,564 tons for the same time in 1909. The world consumption was 4,399,698 tons for the first nine months of 1910, against 3,612,020 tons during a like period in 1909.

In this increase United States interests have taken an active part all along the line. American interests have taken over several nitrate works within the past year, and are negotiating for several more. The use of nitrate has increased very rapidly in the United States during the past few years, the exports thereto having been 120,618 tons for 1907, against 335,722 tons for 1908 and 458,081 tons for 1909.

The outlook seems good for this industry, even at the present low prices of nitrate. The nitrate works that are provided with improved machinery and are run according to modern ideas seem to be prospering, while antiquated methods fail. There would seem to be still good openings for more American capital in this industry in Chile.

The agricultural interests of Chile are using much more nitrate from year to year, with excellent results. The Chilean Government gives special rates on the railways for nitrate as an inducement to the farmers.

WOOD DISTILLATION.

(Preliminary comparative report for 1909 issued by the Census Bureau.)

There was consumed in the United States during the calendar year 1909 in the industry of wood distillation, 1,265,000 cords of wood, as against 978,000 cords in 1908 and 1,282,000 cords in 1907. The average cost per cord reported for the 1909 consumption was \$3.21, which was an increase of 23 cents, or 8 per cent. over that reported for 1908, and of 6 cents or 2 per cent. over that for 1907. While a substantial increase is noted in that branch of the industry using yellow pine, fir, and other soft woods as material, the revival of activity was more marked in hard-wood distillation, due undoubtedly to the material advance in the average value per gallon of wood alcohol over the two preceding years.

While the average value per unit has varied little for most of the products of hard-wood distillation during the past three or four years, for alcohol it has fluctuated over a wide range,

following the passage of the so-called denatured alcohol law, which became effective January 1, 1907. The average value per gallon reported for crude alcohol manufactured during the calendar year 1906 was 34 cents. In 1907 it dropped to an average of 15 cents, increased to 17 cents during 1908, and reached an average of 24 cents in 1909.

The use of sawdust and other mill waste as material in 1909 was substantially greater than in any preceding year, and the indications are that the industry will develop largely in future in the direction of utilizing this class of material.

A comparative summary of the operations in 1909 of the 116 hard-wood distillation plants using 1,150,000 cords beech, birch, maple, etc., and the 31 soft-wood distillation plants using 116,000 cords longleaf pine, etc., follows:

Product.	Hard wood.		Soft wood.	
	Amount.	Value.	Amount.	Value.
Charcoal, bushels.....	53,075,000	\$3,299,000	2,403,000	\$210,000
Crude alcohol, gallons	8,468,000	2,082,000
Gray acetate, pounds..	148,769,000	2,203,000
Brown acetate, pounds	2,157,000	22,000
Iron acetate, gallons..	303,000	28,000
Oil, gallons.....	38,000	3,000	323,000	770,000
Tar, gallons.....	1,365,000	105,000
Turpentine, gallons	683,000	243,000
All other.....	5,000	59,000
Total value.....	7,642,000	687,000

NEW BRITISH ALUMINUM ALLOY.

(From Consul Albert Halstead, Birmingham.)

A Birmingham firm has discovered and patented a new alloy of aluminum, which is called *clarus*, and for which many claims are made.

It is claimed that this alloy is at least 60 per cent. stronger than ordinary aluminum and that its weight is one-third that of brass of an equivalent volume; that it will take a very high polish, equal to that which can be obtained with silver; that atmospheric surroundings do not cause it to tarnish; that castings are not brittle, but can be bent cold; that it is suitable for castings of any size, and that in all circumstances such castings have been found to be sound and free from blowholes and other defects.

It is claimed that the new alloy is excellently suited for automobiles and for electric-railroad, railroad-car, and aeroplane fittings. The manufacturers state that it has been made into sheets, drawn into wire, and into tubes and rods; that they have spun it and stamped it, and that they have made hand-pole brackets for the underground electric railways of London, for railway-carriage fittings, for carriage furnishings, street-car fittings, and automobile and motor-bus fittings.

Cost of Production—Patent Rights.—They assert that it is very little more costly than pure aluminum. Inasmuch as in aluminum alloys much spelter has been used to reduce the cost, the cost of production of this alloy would be greater probably than that of alloys with heavy percentages of spelter, etc. The alloy *clarus* is made from aluminum of 98–99 per cent. purity.

The owners of the patent are prepared to sell the exclusive rights in the United States in preference to permitting its manufacture in the United States under license or exporting the finished product, and are ready to demonstrate its usefulness. (The name of the owners of the patent can be obtained upon application to the Bureau of Manufactures.)

FLAX AND LINSEED OIL.

ENGLAND.

(From Deputy Consul-General Carl R. Loop, London.)

The price of linseed oil in the English market, according to a prominent dealer, changes almost hourly. At the time of

writing (October 25th) the United States is probably buying crude untanked oil from this market or from Germany at about \$11.20 per 112 pounds, in barrels f. o. b. London, less 2½ per cent. for prompt cash.

American linseed oil does not at present participate to any extent in the English market. One dealer advises that it could not have been bought here for some months past, save at a price (c. i. f., London) far in excess of that of English or Continental oil, and adds that it would be almost impossible to make a price here for oil for shipment from the United States.

Crude linseed oil, as supplied from the crushers here, is put up in barrels of about 50 American gallons, in pipes varying from 125–175 American gallons, and also in returnable steel drums of 150–200 American gallons. Linseed oil coming into this country from the Continent is almost invariably sent in barrels, but a part of it is imported in steel drums. Assuming 7½ pounds to be the equivalent of an American gallon, 1 hundred weight (112 pounds) is the equivalent of 15 gallons, and a ton of 2,240 pounds is equivalent to 298 gallons.

The present supply of linseed oil is by no means normal, and has not been during the whole year, the demand far exceeding the supply, and it is said that this situation applies not only to the United Kingdom, but to all parts of the world.

The linseed crop in the United States is just now becoming available for oil; the new crop from Argentina will not be available in the United Kingdom or in the United States until early in the year 1911, while the next Indian crop will not be available for oil until April or May, 1911.

The bulk of the linseed imported into Europe is produced in Argentina and India; small shipments are occasionally made from Russia, and also from the United States, but shipments from the latter have gradually decreased in volume.

The shortage of linseed, both in the United States and Argentina, became apparent at the beginning of the current year, and prices began advancing accordingly, both for the seed and for the oil, until in April a rise in oil of some \$49 per ton (2,240 pounds) had been registered. Owing to various causes, over-speculation included, prices then receded very considerably, but recovered again in August and are now higher than ever, with a difference of no less than £20 (\$97.33) per ton of oil over the prices ruling a year ago. These continued high prices are due to the very unsatisfactory reports regarding the new crops in the United States and Argentina, and if these reports prove true prices will certainly go still higher, and in such case linseed oil in England and elsewhere is not likely to rule below \$195 per ton during next year.

Turning to reliable newspaper statistics for October, 1910, it appears that the ruling price for linseed in London ranges from £45 5s. to £45 15s. (\$220.21–222.64) per ton, while in the corresponding week of 1909 the price varied from £30 to £30 5s. (\$146–147.21) per ton. The importations into the city of London during the week ended October 20, 1910, amounted to 11 barrels from Belgium.

RUSSIA.

(From Consul-General John H. Snodgrass, Moscow.)

The Russian flax crop of 1910 is medium in quantity, but of good quality. The buying price at present (November 1st) is 20 per cent. higher than in 1909, occasioned principally by the larger export demand and the limited stock of the European mills.

During August and September there were few clearances of stocks on account of exporters having succeeded in getting holders to give way in price, but in many places the full asking price was paid. As a rule, dealers have been and are now holding firmly to the little flax they have to sell. A prominent commission house reports as follows:

We are not yet in a position to form a definite opinion as to the

yield compared with last year, taking Russia as a whole, but we are inclined to the belief that the 1910 crop will show a moderate excess. There has been an increase in the total of business carried through in the consuming countries, brought about not by any general buying but by some largish clearances of stocks of certain descriptions, chiefly water-retted; prices have fluctuated to a slight extent, but the last sales reached the highest figures paid. There has been a fair number of transactions in tows; a good deal more would have been done if there had been a greater choice of quality, or if sellers had been more amenable as regards price. A few sales of new crop Slanetz flax have been made at prices which are decidedly under the ideas of the majority of shippers. We have not yet been able to trace any sales of this year's water-retted flax.

The latest official returns show the yield of flax in the several provinces of Russia in the year 1907 was as follows, in tons: Pskov, 32,951; Tver, 64,877; Smolensk, 89,797; Viatka, 47,118; Livonia, 49,568; Vitebsk, 24,989; Perm, 23,931; Kovno, 19,966; Vladimir, 14,485; Kostroma, 16,515; Yaroslavl, 16,182; Mohilev, 16,627; total, 417,006 tons.

CHINESE LACQUER WARE.

(From Vice-Consul Henry Oscar Nightingale, Foochow.)

The manufacture of the lacquer ware known to the Chinese as the "No. 1 Foochow lacquer" can hardly be called an art; it is rather a craft, the result of infinite labor and patience, since the laying on of the coat or color requires no more skill than the simplest form of painting.

This lacquer, although very popular and greatly sought by the Chinese, is little known in America, doubtless owing to a lack of appreciation or the cost, since the market is flooded with a cheap form of lacquer that seems to answer all requirements. The superiority of the No. 1 Foochow lacquer over all other forms is due to its durability and beauty; it takes more time to prepare (in some cases several years) and possesses a finish and depth of color unlike any other products of the same nature. The extreme care taken to refine the pure lacquer, the number of coats given, and the great quantity of gold and silver leaf usually used in the last coat are the cause of this.

Concerning the gold and silver leaf used, one imparts to the lacquer a dull gold color, in whose depth a fine gold powder may be discerned, and the other gives a silver-green effect. Sometimes a little coloring matter is added, but the result is supposed to be better without it. The quantity of gold mixed with the lac is about one-third the selling price for these articles, which usually ranges from \$2-3000.

The earliest record of lacquer is from the Sung dynasty, although it probably existed long before that date but in a more crude form. It was introduced into Japan in the third century from Korea, at the time of the conquest of that country by the Empress Jingo. The seventeenth century marked great progress in the industry in Japan, and the gold lacquer became very popular, but from that time its popularity decreased and the demand did not revive until the last few years. Last year the export from Japan was 219,525 yen. The export of No. 1 Foochow lacquer, though a far superior article, is so small as to be classified in the customs returns under the head of furniture.

The lac, as is well-known, is not a manufactured product, but the sap of the *Rhus verniciifera*, or *Ch'i shu* of the Chinese. The tree is tapped at night during the summer season and the lac sold to the consumer as a dried cake or in a semifluid state. It is first placed in a rectangular pan, where it is continually stirred with a spatula for about two days, then pressed by twisting the lac through a sack made of fine grass cloth and lined with a thick layer of cotton. The refined lac is put into the pan again for a day and the same process is repeated. So prepared, the lac will answer for the first coats given the articles,

but for the final or color coat the lac used undergoes this process four times.

The invention of the No. 1 lacquer is said to belong to the Shen Shao An family, in whose hands the manufacture still is. To this same family is also accredited the invention of silk lacquer.

The term lacquer ware applies only to the thing which has undergone certain preparations before receiving several coats of lac. Ordinary woodwork covered with Ningpo varnish, or even with lac, is not included. The proper lacquer ware may be chiefly divided into two kinds, the ordinary and the silk.

The ordinary lacquer is applicable to almost every kind of furniture and to ornamental articles for the houses, but is commonly applied to woodwork. Only very old wood, usually cedar which will neither warp nor crack, is used for this purpose. Articles and ornaments of the most delicate carving are treated in this fashion. To prepare the woodwork, such as furniture, for lacquer, a lacquerer scrapes the wood 1 or 2 inches wide along any crack or joint or opening that may exist; it is then filled up with lac and two or three coats of linen cloth, which will not only cover the depth but also serve to keep the parts together. After a fortnight or longer, when the lac on the linen is perfectly dry, the woodwork is covered with a thin coat of black lac mixed with a little ching-chu, a kind of clay, the preparation of which will later be described.

Ten days later, a process of general polishing is applied to the article with fine pumice stone of various shapes and sizes. About every ten days a new thin coat of the lac mixture is put on. The article is always polished before receiving a new coat. After the ninth or tenth coat of this black lac mixture, the article is thoroughly polished so as to receive the color coat.

For the preparation of the final coat, a small portion of lacquer that has undergone the refining process four times is mixed by a pallet knife on a stone surface with the gold or gold and silver leaf. When thoroughly mixed, it is placed in the center of a thin sheet of cotton paper. The paper is then rolled together with the lacquer inside, the ends being twisted in opposite directions, until the lac oozes through. This is repeated three times. There is great waste by this process which may also account for the price charged for some of these articles.

There is but one coating made of this lacquer. Sometimes a flat surface is decorated by adding flowers or birds with ordinary paint, but this is not very popular, since the color and quality of the lacquer itself are deemed sufficient decoration.

The silk lacquer is generally applied to small articles either for practical use or for ornamental purposes, such as vases, card cases, and images.

The art is so far advanced that images of almost every description can be made under this system, with accuracy and clearness. The process commences by pasting a coat of native printing paper with rice glue mixed with ching-chu powder on a well-modeled clay image, care being taken to cut the paper into proper sizes to suit the different parts where it is pasted, and to paste it so neatly that every wrinkle of the face or fold of the material, should there be any, will remain clear cut. After the pasting, the figure is thoroughly washed with this thin mixture and left to dry for two or three days.

On top of the paper is then pasted the silk with a plaster of black lac and pulverized ching-chu, with still greater care as to the overlaps and folds than is required in the paper coating. Ten days later another coating of silk is added after the necessary polishing has been applied.

For small articles only two coats of silk are sufficient, but in the case of larger ones one or two more coats may be added. When the silk molding is dry and carefully finished subsequent coatings of black lac mixture are applied thereto at an interval of about every ten days in the same manner as to the wood, only greater care is exercised and longer time spent in the

polishing. Before receiving the color coat the image is immersed in water for such a length of time that the clay inside will dissolve and can be taken out through a hole left at the bottom of the figure for that purpose. After the removal of the clay the opening is sealed and a fortnight later the hollow and exceedingly light article is ready to receive its decoration.

On silk as well as woodwork the color coat is applied but once. The lac, though black itself, can be made almost into every color existing, and of various shades, by mixing it with other ingredients. The most costly colors are those which contain the greatest quantity of gold dust, and the colors in most common use are bronze or other green of various shades, and liver-purple or dark maroon-gold.

The term gold lacquer is easily misinterpreted to mean lacquer ware sprinkled with gold dust or fragments of gold foil or inlaid with gold thread, etc. In gold lacquer the gold or silver has been pulverized so fine that it appears no more as sprinkled dust, but its richness is blended with the other coloring matter and the refined lac giving a lustrous and lovely tint of a uniform shade.

The lac in the ching-chu mixture used for the primary coating has passed the refining process only twice instead of four times, as is described in the foregoing for that of the last coat. A little water is added to the lac when it is being mixed with the pulverized ching-chu. Ching-chu is a refined red clay. It is dissolved in water, and after the impurities, such as sand, have been removed, the muddy water is filtered through certain layers of paper and porous tiles. The fine clay found on the top of the paper is dried into tablets or bricks, in which form it is sold at the market. This pulverized clay mixed with the lac will form a crisp coating on the woodwork or harden the silk in the silk lacquer.

A genuine No. 1 Foochow lacquer will stand any climate and any amount of washing, even with boiling water. In the common form of lacquer unrefined lac is used for the primary coating, and that for the color coat has not been refined more than twice. Instead of ching-chu, which is comparatively expensive, the powder of broken bricks and tiles is freely used. The color lac is very seldom or never enriched with pulverized gold and silver. Linen is substituted for silk. Very little or no polishing is done in each and every interval between the coatings, until before the last coat.

Owing to cheapness, there is much greater demand for the imitations than the genuine. Ordinary lacquer ware will receive on an average but five coats, whereas No. 1 never less than nine and sometimes as many as twenty. (Seven photographs accompanied the foregoing report and will be loaned to interested firms on application to the Bureau of Manufactures.)

OFFICIAL REGULATIONS AND RULINGS.

Only a few of the more important rulings are reported here. For others the reader is referred to the publications of the Board of Food and Drug Inspection and to Treasury Decisions.

FOOD INSPECTION DECISION NO. 129.

The Certification of Straight Dyes and Mixtures under Secondary Certificates. (Amendment to F. I. D. 77.)

In Food Inspection Decision 77 provision is made for the recertification of straight dyes (*i. e.*, the seven accepted dyes of F. I. D. 76) and mixtures thereof, with or without other harmless ingredients.

Doubt has been expressed as to whether the requirements of F. I. D. 77, with respect to certification, are the same for those who are not manufacturers as they are for manufacturers. This amendment is issued relative to recertification in order to remove uncertainty and to indicate the scope of F. I. D. 77.

All persons, manufacturers or others, requesting certification of mixtures or recertification of straight dyes, or of mixtures

or combinations thereof, shall submit the following form of secondary certificate to the Secretary of Agriculture:

SECONDARY CERTIFICATE.

I,, residing at, do hereby depose and state
(Full address.)

that I have repacked lbs. of certified lot (or lots)
purchased from, of

This repacking has been accomplished in the following fashion:

.....
(Full description of what has been done with the lot or lots.)

Certified mixture No. J. D. & Co., or certified straight
dye No. J. D. & Co.

(Name.)

Trade name

Subscribed and sworn to before me,, in and for the
of at, this day of

.....
(Name of officer authorized to administer oaths.)

When the secondary certificate refers to mixtures, the term
"mixture" means:

not only such mixtures as consist wholly of certified coal-tar dyes but also those which contain one or more certified coal-tar dyes (and no other coal-tar dye or dyes) in combination with other components, constituents or ingredients not coal-tar dyes, which other components, constituents, or ingredients are in, and of, themselves or in the combination used harmless and not detrimental to health or are not prohibited for use in food products; the exact formula of such mixtures, including all of the components, constituents, or ingredients, or other parts of the mixture, together with a statement of the total weight of mixtures so made, must be deposited with the Secretary of Agriculture. (F. I. D. 106.)

The term "straight dye," as used herein, refers to the seven dyes specified in F. I. D. 76.

In the case of mixtures one (1) pound samples, and in the case of straight dyes one-half ($1/2$) pound samples must be submitted with the secondary certificate. If larger samples are needed in individual cases the Department will ask for them.

Only those mixtures will be certified which contain no other dyes than coal-tar dyes previously certified. Mixtures containing animal or vegetable dyes are not subject to certification.

The above form for secondary certificates varies but slightly from that given in Food Inspection Decision No. 77. It contains the addition "Certified mixture No. J. D. & Co." and "Certified straight dye No. J. D. & Co." When the manufacturer or other person submits a secondary certificate, whichever legend is appropriate to the certificate is to be used. The initials are to be those of the person or firm filing the certificate; the blank space is to be filled with the number of the secondary certificate filed by that particular person or firm. For example, the firm of J. D. & Co. has already filed fourteen secondary certificates, the new one to be filed under the form given above will then be labeled "Certified mixture No. J. D. & Co. 15," or "Certified straight dye No. J. D. & Co. 15," as the case may be; that is, the recertified straight dyes or certified mixtures are to be given a number in regular order, according to the number of such secondary certificates filed by any person or firm. The completed legend is the one to be used in marketing the products thus submitted under the secondary certificate. Notification will be given of the acceptance or rejection of the certificate when investigation of the product has been completed.

Makers of secondary certificates must submit the trade name of mixtures produced, and no such trade name or keyed modification thereof should be used on any other mixture prepared by the same person or company.

Secondary certificates are to be sent in duplicate to the Department of Agriculture; the duplicate need not, however, be signed or sworn to. The samples should be submitted with the secondary certificates.

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY

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No. 2

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EDITORIALS.

CHEMICAL ENGINEERS IN THE TEXTILE INDUSTRY.

In the textile industry there is a considerable need of the services of chemical engineers with some special training along the lines of textile manufacturing. For the usual type of analytical chemist, such as is turned out in such large quantity by so many of our colleges and technical schools, there is very little future in a textile mill.

In the various operations of manufacturing textiles, there are many occasions where the knowledge and advice of a trained chemist would be desirable. This is especially true in operations involving dyeing, bleaching, mercerizing, carbonizing, finishing, printing, sizing, scouring, etc. But something considerably more than a general knowledge of chemistry is required: even skill in analytical chemistry will not be of much avail. A textile chemist needs to be adept in engineering, to have a knowledge of machines, their principles of construction and operation, to be able to solve problems in the application and distribution of power, to devise methods for the handling of large quantities of liquids, and the preparation and conveyance of solutions, to be able to follow up main products and by-products, and to be able to work out problems involving economy and efficiency and the utilization of waste products.

This seems rather a broad curriculum, when it is also understood that at the basis of all this there

must be a broad and substantial knowledge of both general and applied chemistry, and furthermore there must be a specialized knowledge of the textile fibers, and the various operations and treatments to which they may be subjected.

In this country, there does not seem as yet to have been a successful affiliation of studies in chemistry and engineering as evidenced by the courses offered in classes in chemical engineering at a number of our colleges. Why these combinations of studies are not popular among the students and why such branches do not draw the efforts of the best type of student is hard to say. Probably the fact that chemical engineers are not a factor in the teaching force has much to do with this lack of development of this branch of study in this country.

In our textile schools, while considerable teaching is offered in the specialized subjects of textile chemistry, with more or less attention paid to practical instruction, there is, on the other hand, a lack of thorough and broad training in the general principles of chemical science. The product of the textile school, therefore, has a short-sighted chemical vision, and this produces lack of initiative in after life. While some of the textile schools affect to train their students in the principles of engineering, the courses they offer are more or less amateurish and raw, a result which is more inclined to give the student a good opinion of himself than to turn him out an efficient chemical engineer.

The best course for a student to pursue, who desires to become a highly developed and efficient textile chemist, would be to pass through as good a course in chemical engineering as it is now possible to obtain at college, then specialize for a year or more at a textile school, taking not only in this connection the studies in dyeing, bleaching, textile chemistry, etc., which may be available, but also studies relating to the grading and selection of stock, and the principles underlying the processing of the fibers in the preparation of the finished fabric, such as carding, spinning, and weaving. After such theoretical knowledge is thus acquired, the prospective textile chemist should seek employment in a mill where he may have access to as wide an experience as possible. He should not be content to go into the mill laboratory (if there is one) and perform routine analyses merely; such work should be only a part of his functions. He should work out in the various departments of the mill, put on overalls and get his hands soiled, but acquire a knowledge of the practical manufacturing operations all through.

With such an equipment and experience, a man may become a highly efficient textile chemist. For such there are plenty of excellent opportunities for

rapid advancement and high salaries. For the young man who is content to remain in the laboratory at the routine practice of analyses and thinks the dye-house is too nasty a place to work in, there is seldom any place beyond twelve to fifteen dollars a week salary. For the other kind of man, however, his future is only limited by his personal initiative and energy.

J. M. MATTHEWS.

ORGANIZATION FOR ROUTINE WORK.

No more careful and painstaking work is required in any branch of chemistry than in the design and organization of the laboratory which turns out large numbers of routine analyses, requiring skill and accuracy, in a short period of time. On such control analyses the successful operation of innumerable large industries depends and the more accurate the work and the more rapidly it is turned out, the better the control will be. It appears that any chemist of average ability can make one or a small number of analyses and report reasonably correct results. But with the multiplication of samples and the making of hundreds or thousands of analyses, it appears almost unavoidable that a certain percentage of incorrect results are reported. In the abstract one might expect that the more samples analyzed, or the more determinations made the less would be the chance for error in any individual case. Practically this is seldom true. The steel-works laboratory probably takes first rank as a routine laboratory and will continue to do so, but the fertilizer laboratory has become a close second on account of the immense increase in fertilizer manufacture. In these laboratories, the organization for routine work has reached a rare degree of refinement, but perfection and even a perfectly satisfactory condition of affairs has not yet been attained. The average chemist, upon leaving college, looks upon routine work as a thing to be shunned or at most as a line of work to be followed only temporarily, and used as a means to other ends. Great emphasis has been laid on this view of the case recently by college professors and industrial chemists. It is needless to say that there is a possibility if not a danger of overemphasizing this side of the argument. Let us pause for a moment to say a good word for the skilful, painstaking analyst whose results can be relied upon for the control of large manufactures. In spite of the view taken of routine chemical work by the profession at the present time, such work is highly appreciated by at least one man—the works manager or superintendent. We believe that as time goes on this sort of work will receive greater recompense than it does now, recompense more in proportion to its importance in the operation and control of great industries.

In passing we may say that whatever our views on the subject may be, we can be permitted to admire the excellent equipment, organization and management of such a routine laboratory, as the nitrogen laboratory in the Bureau of Chemistry at Washington. It is a pleasure to inspect this laboratory and to see

under what satisfactory conditions routine work can be conducted.

THE FERTILIZER INDUSTRY.

The steady and consistent growth of the fertilizer industry and the greatly increased use of fertilizers during recent years indicate a very large future for this branch of manufacture. The new soils in this country have for the most part been taken up—many farms have been “used up,” many farms abandoned. As the old farmer explained to the Professor of Agriculture who was lecturing in his district: “You can’t tell me anything about farming. I’ve used up three farms.”

One of the most important practical facts in regard to the use of fertilizers is that they are used chiefly in the older settled parts of the country and where the same crop is raised year after year. Be the explanation what it may, the facts and the experience of many different individuals appear incontrovertible. The tendency now appears to be toward an increased use of fertilizers even on the newer soils, and all must agree that this tendency is a wholesome one. In the meantime the large fertilizer manufacturers are constructing factory after factory and mixing plant after mixing plant and the growth in output year by year is enormous. The old and tried sources of nitrogen, phosphorus and potassium are the ones chiefly drawn on for the increased consumption. In spite of the agitation for raw phosphate rock as a source of phosphorus, acid phosphate continues to be the principal phosphatic fertilizer. Air-nitrates and cyanamide are making headway slowly on account of the large supply of Chili saltpeter. Conservationists have issued a warning on the subject, but there appears to be no immediate danger of a shortage in the supply of fertilizer raw materials. The large increase in the use of commercial fertilizers is the more interesting, because of the fact that there has been a corresponding large increase in the use of green crops, legumes and barn-yard manure on the farm. The increased use of commercial fertilizers has come in addition to a largely increased use of the natural fertilizer resources of the farm. We are, beyond question, progressing gradually toward permanent systems of agriculture.

INDUSTRIAL RESEARCH.

Since the first metallurgist, by making such simple tests as were in his power, investigated the suitability of various earths for making iron, or since the ancient Egyptian glass-maker examined various alkaline salts which might be adapted to his art, industrial chemical research has ever been the guiding light of chemical industry. Called by various names at various times, whether it rested upon ungeneralized empirical knowledge, or whether through the vitalizing force of science, it assumed the voice of prophecy, fundamentally it has always been the same. Like the pillar of fire of old its purposes has been to lead and guide. It has guided all-conquering industry out of the bondage of tradition and led it from goal to

goal and conquest to conquest until the observer, with any knowledge of the history of industry, can scarcely conjecture whither the next advance will lead. This progress can not properly be compared to finite geographical explorations and discoveries; it is more like the exploration of space and the infinite worlds of space.

The chemical investigator connected with the industries has been likened to the exciter on an electric generator, while the superintendent or works manager, the driving force, has been compared to the generator itself. There appears to be much truth expressed in the simile. Each is necessary for the development of the power required to operate the plant. There is an implied truth also apparent, namely, that the scientific imagination is not usually accompanied by the capacity to organize and to operate a large industry.

The present age is one of industrial transition, wherein the scientific man is beginning to have a more prominent place in industry than previously. That he does not come to the front more rapidly and take the place to which he believes he is entitled is sometimes a cause for complaint on his part. However, it has been demonstrated again and again, that so far as the mere traditional operation of a plant is concerned, the accumulated experience of years or hundreds of years, is of more value than the theoretical contributions of the scientific man. The chemist, for example, must usually spend a number of years in studying present-day practice in an industry, before he can really be of much service to that industry. The training of most superintendents and works managers is such that the development of their imagination is neglected or retarded. They lack the imagination necessary to carry the operations of their factories beyond present-day practice. On the other hand, the college-trained chemist usually has too much imagination and too little common sense and knowledge of present-day practice. Possibly, also, he has too little desire to investigate thoroughly present-day practice before undertaking to revolutionize it, and herein are the sources of the eternal conflict between the practical man, educated by experience, and the college-educated man. Once in a blue moon comes the chemical engineer—that rare combination of chemical and engineering instincts. And rarer yet is the college-trained man who makes a satisfactory chemist, engineer and superintendent. Most plants must be satisfied now and probably in the future with a separation of these offices, and perhaps the highest results may be accomplished by a proper coördination of the work of chemist, engineer and superintendent.

Whatever the solution of the much tortured question, industrial research will go on. Such research may be far removed from immediate application. As Dr. W. A. Noyes has suggested, Kekulé's ring formula for benzene lies at the bottom of much of the coal-tar industry. Or it may directly start into being a new industry, like Acheson's discovery of carborundum. Again it may result in improving or revolution-

izing the old methods of an industry, like Bessemer's discoveries in steel-making.

To foster such work in every possible way and to spread among scientific co-workers and mankind generally the knowledge of such inventions is the best work that a scientific society can perform.

CRYOLITE AND ITS INDUSTRIAL APPLICATIONS.

BY ALFRED S. HALLAND.

Received December 1, 1910.

While the mineral cryolite has become almost indispensable in certain branches of the chemical industry, yet it cannot be called one of the important minerals in a commercial sense. It is, however, of interest in a chemical and geological sense. In the following paper the writer will try to outline its general characteristics, its applications in the arts, and finally the methods used in bringing it from its crude state into the almost chemically pure condition in which it is brought on the market.

I. Source.—The only place in the world where cryolite has been found in considerable quantities is at Ivigtut, an esquimaux hamlet on the southern coast of Greenland at 61° northern latitude. Minerals of a similar composition have been found at Pike's Peak, Colo., but not in quantities to pay mining. Cryolite was first introduced to the scientific world about the year 1800. The esquimaux at Ivigtut had for centuries back known and valued the beautiful white mineral; they used to grind it and use it for snuff. The first imperfect analysis of it was made by the Danish chemist, Abildgaard, who gave it as containing acid of fluorspar, alum and some plant ash (potash). Its true constitution as a double salt of sodium fluoride and aluminum fluoride, $3\text{NaF} \cdot \text{AlF}_3$, was first established by the analysis made by Berzelius in 1823. The first crystallographic description of the mineral was given by the Portuguese mineralogist, D'Andrada e Silva; he gave to the mineral its present name, cryolite, which is Greek for ice stone, because pieces of cryolite when viewed under water show a strong resemblance to ice. The crystal form is monoclinic and the hardness relatively low, 2.5. Cryolite is difficultly soluble in water (about 1:3000) but quite soluble in warm solutions of aluminum salts, preferably aluminum chloride. This furnishes an excellent means of separating it analytically from quartz. When finely powdered cryolite is stirred in water it appears to dissolve therein; this is due to the fact that cryolite has almost the same refractory index as water. In its natural state cryolite is more or less heavily intermixed with other minerals, mostly ironspar (siderite), zinc blende, galena, chalcopryrite and hagemannite. The color of the cryolite itself is generally a pure white but sometimes smoke-colored pieces are found, and it never fails that in the smoke-colored parts are found well-developed crystals of red fluorspar. This red fluorspar was first examined by Julius Thomsen, who obtained interesting results. He found that it contained a small quantity of yttrium

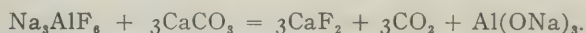
¹ Paper read before the Western New York Section of the American Chemical Society at the University of Buffalo, Nov. 3, 1910.

fluoride and further that by heating it gave off helium while emitting a yellow light. Radium was not known at that time, but after its discovery this red fluorspar was tested for radioactivity and found to possess it in a much smaller degree, however, than pitchblende. This explains why helium is obtained by heating the fluorspar. The dark color of the surrounding cryolite is the effect of the emanation on the mineral. Both the coloration and the radioactivity disappear on heating to a low red heat.

The foreign minerals following the cryolite are shortly described. Its constant companion is the ironspar which at times makes up 20 per cent. of the entire weight. It is found in very well-developed, beautiful brown crystals, at times very large. Next in quantity follow galena, zinc blende and chalcopyrite. Quartz is always found in small quantity and is, of course, hard to distinguish from the white cryolite.

The cryolite deposit at Ivigtut is practically one solid mass, located right under the surface of the earth. The length of the deposit is about 600 feet, running parallel with the coast, and the width about 200 feet. The depth of the mine which is nothing but an open cut is now about 150 feet. While the surface extension of the deposit as seen is comparatively small, the deposit fortunately widens, the deeper one descends; and the depth of the deposit is unknown. There is therefore no reason to fear that the mine will become exhausted for a long time. Considerable discussion has been going on as to the origin of this extraordinary deposit. The theory now generally accepted is that the cryolite is of volcanic origin and at one time was fluid. This idea is strongly supported by the fact that big pieces of granite from the surrounding rock occasionally are found embedded in the cryolite. This excludes the possibility of the cryolite having been separated out of a watery solution, as the granite boulders would have fallen to the bottom in that case. On the other hand, it is difficult to explain the presence of crystallized ironspar, ferrocarbonate, which decomposes entirely at a temperature below the fusing point of cryolite (about 900° C.). One must assume that the cryolite, like other eruptive masses, contained water and carbonic acid gas and was subjected to an enormous pressure. It is therefore reasonable to suppose that the fusing point of the cryolite was considerably lower, and the decomposition temperature of the ferrocarbonate higher. That the cryolite originally solidified at a great depth and later came to the surface can be judged by the nature of the surrounding rock of granite and porphyry.

II. Cryolite Soda.—The first successful attempts to utilize cryolite were made by Julius Thomsen in 1852. He tried to win from it soda and alum—two materials which were at that time considerably higher in price than now. Thomsen found that by heating cryolite with limestone the following reaction took place:



When the mass is extracted with water, the sodium aluminate goes into solution, while the calcium fluoride remains undissolved. Now by conducting carbonic acid

gas into the sodium aluminate, hydrate of aluminum and soda are formed.

$$2\text{Al(ONa)}_3 + 3\text{CO}_2 + 3\text{H}_2\text{O} = 2\text{Al(OH)}_3 + 3\text{Na}_2\text{CO}_3.$$

This, the cryolite soda process, was carried out on a large scale in the following manner: The finely ground cryolite which need not be pure (in fact the presence of sulphur compounds which by the subsequent treatment would form glauber salt would make the soda crystals come out hard and distinct) was mixed with lime and heated in a sort of reverberatory furnace. The mass was leached with water systematically, finally giving a solution of aluminate 33° Bé. strong, into which carbonic acid gas from the flues was led. The hydrate fell out in a granular condition, which made filtration possible. The solution of soda was evaporated to crystallization. Originally the aluminum base was transformed into aluminum oxide but was later worked into sulphate of aluminum. The by-product, calcium fluoride, was dried and sold to the bottle-glass factories. Several cryolite soda plants were built in Europe on the plan of the mother factory in Copenhagen. They were operated with several ups and downs for about 15 years. At that time the Solvay process came into use and soon triumphed over the other soda processes. The rights for the United States were acquired by the Pennsylvania Salt Mfg. Co., which built a plant at Natrona, near Pittsburg, and here the process was worked much longer than in the old world on account of the heavy duty on alkalis in the United States.¹

III. While the use of cryolite for production of soda and alum, therefore, must be said to be a thing of the past, other important applications developed, *viz.*, for opaque glass (so-called milk glass), for the enameling of iron ware and in the metallurgy of aluminum.

In order to produce white opaque glass, several materials, mainly bone ash (calcium phosphate), fluorspar and tin oxide, have been and are still used as an addition to the molten glass. Superior to them all in producing a pure white and uniformly opaque glass is cryolite. The amount necessary is about 10 per cent. of the weight of the glass; it is added to the flux in which it dissolves easily. On cooling the glass the cryolite separates out in minute crystals throughout the mass, which causes the opaqueness.

The enamel industry consumes a great deal of cryolite. While it is useful as an ingredient of the enamel for cast-iron goods it is mostly used for pressed steel articles. The enamel for this purpose is made up from feldspar, quartz, soda, borax, etc., which are mixed together, fused, ground, and stirred to a fine paste with water; this is now applied to the object and fused on in an oven. The above-mentioned materials, however, will produce a transparent enamel through which the dark color of the steel is visible, making the enamel appear a bluish gray (well-known from the "granite" household ware), but if 5–10 per cent. cryolite is added to the enamel flux a pure white, totally non-transparent enamel results. By adding smalt to the flux the well-known

¹ The writer believes that pure aluminum oxide for the manufacture of aluminum is still manufactured at Natrona by the cryolite soda process.

blue, non-transparent enamel is obtained. Cryolite enamels are not poisonous; this is a feature which strongly recommends their use for kitchen utensils. Fluorspar will, to some extent, produce a similar effect but it renders the enamel difficultly fusible. An interesting substitute for cryolite for use in enamels has lately appeared in Germany. It is sodium fluosilicate, Na_2SiF_6 , which now can be obtained very cheaply as a by-product from the phosphate fertilizer works. When treating certain natural phosphates with sulphuric acid, silicon fluoride, SiF_4 , escapes. The German factory law would not permit this gas to escape into the air and the fertilizer works were compelled to absorb it in water. From the watery solution of H_2SiF_6 thus formed the sodium salt is obtained by neutralization with caustic soda. The sodium fluosilicate mixed with bauxite is sold as a substitute for cryolite. It does not do as good work, however, and does not effect any considerable economy as it loses 30-40 per cent. of its weight on fusion.

The role of cryolite in the aluminum production after Héroult's method is well known. Here the fused cryolite forms the dissolving bath for the bauxite, which is the actual electrolyte. As the electrolysis proceeds, bauxite is added to the bath. The amount of cryolite used for the production of 10 kg. aluminum is about 1 kg. It is important that the cryolite for this purpose should be as free from quartz as possible as the electric current separates silicon from any silica present which alloys itself to the aluminum, making it brittle.

One more application of cryolite should be mentioned, namely, for the production of white Portland cement. The following is an extract from the *U. S. Geological Survey Report, 1909*: "The white cement.... is not used as a structural cement, but rather for ornamental purposes. Raw materials suitable for white cement are not widely distributed and must be selected with great care; silica and alumina must be properly proportioned and iron oxide must not be present to exceed 0.2 per cent. With the use of materials low in iron it has been found essential to add an iron-free fluxing material which shall perform the function of the iron in effecting combination between the silica and the alumina. In one of the white non-staining cements manufactured in the United States under patent rights, 2 to 5 per cent. of cryolite is the material used as a flux."

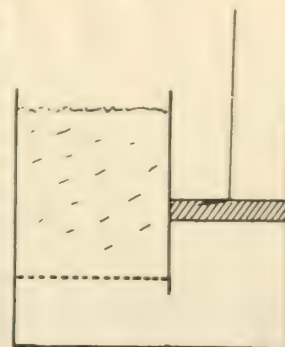
IV. Purification of the Cryolite.—It is obvious that the cryolite as it comes from the mine must be freed from the accompanying minerals before it can be used for any of the purposes mentioned. A rough idea of how this is done will be given in the following:

The first operation consists in breaking with a plain sledge hammer, and already at this point a great deal of pure white material is sorted off. The mass of impure pieces is conveyed to vibrating screens which sort it into 4 different sizes, from the size of a hand to that of a wheat grain. The big pieces down to the size of a walnut are now treated separately; they are placed on a circular anvil, 1 decm. in diameter, on top of which a mechanically driven chisel is working.

Several such chisels are placed in a battery along the same desk. The pure parts are separated in this manner, while the im-

pure parts, still containing considerable cryolite, are mixed with the small material from the vibrating screens and brought onto another set of screens which separate the mass into two sizes, from 14 mm. to 1 mm. and from 1 mm. down to the finest dust. These two products are now worked up separately, but according to the same principle, which is first a separation according to specific gravity and next a magnetic separation.

Fig I.

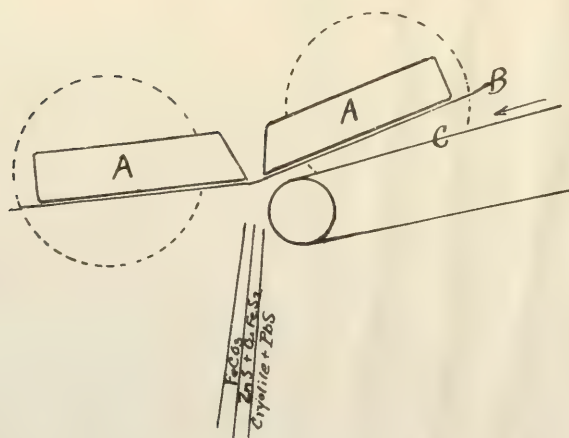


The separation by specific gravity is done in so-called jigs—appliances with which any metallurgical engineer is familiar. A jig is a square water tank divided by a vertical wall into two compartments which communicate at the bottom. The bottom of one compartment is a wire sieve, onto which a stream of water leads the mixture of minerals to be treated. In the other compartment is placed a plunger which is moved up and down with quick strokes by an eccentric. At each downward stroke a quantity of water is driven from the plunger compartment into the adjoining one and up through the sieve. The mass of minerals is hereby lifted from the sieve and left in suspension for a short period, and after a number of strokes the heavy minerals will settle to the bottom while the lighter ones, in our case the cryolite, will gather on top. Several jigs are placed in steps in series and the running water brings the material from one jig to the next and finally off the jig. Two products are ultimately obtained in this manner, one containing almost entirely cryolite and one the gangue minerals with some cryolite. They are both dried and are now ready for the magnetic separation.

Magnetic mineral-separation is based upon the fact that different minerals show a different permeability for magnetic lines of force. If a mass of mineral fragments of approximately the same size is made to drop through a magnetic field the lines of force will concentrate in them in varying intensity according to their permeability (or their "magnetism") and they are consequently attracted more or less towards the poles of the magnet. This causes the curve of their fall to deviate more or less from that of the vertical line determined by gravity, and a separation and collection of the different minerals is thereby made possible. The magnetic ore separators were originally devised and are still mostly used for the enrichment of low-grade magnetite ore. For this purpose a comparatively weak magnetic field is employed on account of the great permeability of the magnetite, but in the case of cryolite-separation a very strong field is necessary. Cryolite, galena and

pyrites are totally impermeable; chalcopryrite and zinc blende possess a very small permeability and iron-spar a considerably greater, although much smaller than that of magnetite. The arrangement used in cryolite-separation is roughly sketched in Fig. 2. The two leveled poles A of a very strong electromagnet are placed above a felt cloth, B. An endless belt, C, carries the mixture of minerals into the magnetic field. Cryolite and galena drop straight down as soon as they leave the belt, while zinc blende and chalcopryrite go a little further and drop into a separate

Figure 2.



slit. The iron-spar goes still further and is gathered through a third channel. There is always a small amount of magnetite present, which by and by would stick in a solid mass to the felt cloth and interrupt the work if not removed. This is done by passing the mass of minerals previously through a *weak* magnetic field. The first product from the jigs yields after this separation a pure cryolite, while the second product yields a mixture of cryolite with some galena. A following jiggling separates them completely.

The purified cryolite is either sold in lumps or ground to a fine powder on a chaser mill. A careful grinding allows here a separation from a small amount of quartz still present, as the quartz is not ground so easily and can be removed by a subsequent sifting.

The separated gangue minerals possess some value. The iron-spar is sold to steel plants and the galena and chalcopryrite which contain traces of silver and gold respectively go to a smelter.

It would probably not pay to subject a cheap mineral to such a complicated treatment as that above described, but cryolite is relatively high-priced—it sells around \$160 per ton. The cryolite-separation as described is to the writer's knowledge only carried out at the "Oresund Chemical Works," Copenhagen, Denmark.

ON THE INTERPOLATION METHOD OF OIL ANALYSIS.¹

By J. J. KESSLER AND G. K. MATHIASON.

Received December 14, 1910.

The methods of analyzing oil mixtures may be reviewed under three divisions:

First.—Those methods which depend upon a separation of the constituent oils, or their derivatives.

Second.—The qualitative identification of one oil in the presence of another, by means of color reactions, odor, etc.

Third.—The determination of some of the physical constants of the mixture of oils and the use of such data in drawing conclusions as to the percentage of each constituent present.

Of these three general methods, the first one, by far the most satisfactory in principle, has unfortunately very limited application. A separation of the constituent oils is many times either impossible or impractical.

The constituent oils of a mixture are generally soluble in one another in all proportions at ordinary temperatures, and separation by fractional crystallization is not possible. Again, the oils are more or less decomposed by distillation, and a clean separation is, except in very special cases, impossible.

As an illustration—hydrocarbon oils may be separated from ester oils by saponification, but, of course, the method is limited to those cases where hydrocarbon oils are present.

The second set of methods, the qualitative identification of one oil in presence of another, by means of reactions producing characteristic colors, while of the very greatest qualitative value, has very limited application. Many such color reactions will be recalled.

Among the most valuable are the Liebermann-Storch reaction for the identification of rosin oil, rosin and cholesterol, the Bechi, Halphen and Brullé tests for cottonseed oil; the Villavecchia test for sesame oil, etc., etc.; of very limited usefulness are the color tests with nitric and sulphuric acids.

The only method of perfectly general application, the third set of methods, may be called interpolation methods, because one calculates a percentage composition from certain physical constants of the mixture, after assuming values of the corresponding constants for the pure oils. The inherent weaknesses of such procedure need only a rapid review. The first and greatest difficulty lies in the fact that a commercial oil, whether a mineral, a seed, an animal or a fish oil, has an individual character, depending upon the condition of the source of the oil, the method of obtaining the oil, method of refining, of storing, the age and the conditions under which the oil is kept. The fundamental necessity of exact interpolation is, therefore, lacking. We ought to know the particular constants of the particular oils in the mixture in order to obtain exactness, and this is impossible.

Our literature does not give us the assistance that it should in this respect. It is too general. Lewkowitsch, for instance, will give us constants from

¹ Read before the St. Louis Chemical Society, May 9, 1910.

different observers, working at widely different periods, on oils of continental or British origin, and which have been obtained by methods differing widely in details. We ought to have, on the other hand, tables showing constants for the oils actually on the American market, which constants have been obtained by standard methods. We are now beginning to get such information.

The cottonseed oil literature is very extensive; so is that of linseed oil, and the government bulletins are of the very greatest service both as to standardization of methods and the compilation of up-to-date analytical results. No doubt, the time is near at hand when we will be able to get the best of such work collected together and easily available.

A second difficulty lies in the fact that the constants of many oils have approximately similar values, while the precision of an interpolation of any sort depends partly upon the condition that one variable changes rapidly for a correspondingly small change of the other.

A third difficulty lies in the very generality of the method. The physical constants obtained may apply equally well to many different mixtures. A gravity of 0.920, for instance, does not define any particular oil or mixture of oils. It must be used with other data in enabling the oil chemist to proceed with the logic he uses in reaching his results.

From the foregoing is seen the difficulty of obtaining an exact analysis by the interpolation method.

On further consideration of the requirements for exact interpolation, we must not forget one very important point, a point next in importance to the requirement of having exact end points. This point is not mentioned nor discussed in works on oil analysis, and while we cannot believe that it does not occur in many places in some of the many papers that have been written on the subject, it is certainly not a part of the general literature.

The requirement referred to is that the form of the functional relationship between composition on the one hand and property on the other shall be known.

Geometrically this means, of course, the determination of the shape of the curve joining the two end points, or, if three oils are present in the mixture, the shape of the surface joining the three end points. As stated, we do not find any explicit statement on this question in the general works on oil analysis. The inference of the chemist is, we believe, that the curve is a straight line.

Stillman¹ gives a formula for calculating the composition of a mixture of two oils, after assuming the kinds of oils present, their Maumené test, and using the observed Maumené test.

This formula is based on the assumption that the temperature rises of a mixture of oils is proportional to the temperature rise of the constituent oils, and the relative amounts present. It is assumed here, therefore, that the relationship is additive, that the law of the mixture of oils, as far as this test is concerned, is a straight line.

We wish to present some experimental data on this point. Our plan of work has been to take certain commonly used oils, make mixtures of them, obtain constants on these mixtures, and plot the results against the composition, in order to obtain an insight into the law of the mixture.

The oils used in this work were castor oil, cottonseed oil, linseed oil, a rosin and a mineral oil. The rosin and mineral oils were selected with reference to their having viscosities similar to those of linseed and cottonseed oils, such oils, in other words, as might be used in the adulteration of linseed or of cottonseed oils. Some care was used in selecting these oils, in order to be sure that the oils were in the first place pure oils, and in the second place, that they were representative oils; that is, that their constants were average constants. In each case the oil was obtained in a barrel quantity, and bore the name of the crusher, or refiner.

The castor oil was a No. 1 castor oil, and was obtained from the Waters-Pierce Oil Company. The barrel bore the label of the Robert B. Brown Oil Company. The linseed oil was obtained from the American Linseed Co., direct from their warehouse. It was designated as "Pure Pressed Raw Linseed Oil—Old Process." The cottonseed oil was obtained from the Proctor & Gamble Co. It was designated as "White Clover Cooking Oil," and was a summer-bleached oil. The mineral oil was obtained from the Waters-Pierce Oil Co. It was designated as "Paraffine Oil." The rosin oil was obtained from the American Naval Stores Co., and was shipped to us direct from Savannah. It was designated as "No. 2 Rosin Oil."

Our method of working was to make up approximately 1000 gram samples, by direct weighing of the constituents. We made seven different mixtures of each set of two different oils. The percentages chosen were 2, 5, 20, 50, 80, 95 and 98 per cent. It will be noticed that our observational points were chosen unevenly along the composition line, in order to crowd our observations near the end points. This was for the purpose of enabling us to study the influence of a small quantity of one oil in another. We made up, therefore, combinations of five oils, two at a time, each of which were made up in seven different mixtures, or seventy different samples in all.

The tests that were studied were as follows: The acid No., saponification No., density, flash test, together with the fire test, Maumené test, and viscosity at 70° F. The saponification No. and viscosity were made in duplicate in each case, and the other tests in duplicate where the results showed a larger accumulation of experimental error than was considered allowable. In some instances where the acid number was very small in both members of a mixture, the determination was omitted for that particular mixture.

The methods used for making the tests named were as follows:

Acid No.—Ten grams of the sample were weighed into an eight-ounce oil bottle. 20 cc. 95 per cent. ethyl alcohol were added and the mixture shaken thoroughly. The mixture was titrated with *N*/10

¹ Edition 1900, "Engineering Chemistry."

potassium hydrate solution, in water, using phenolphthalein as an indicator. Blanks were run on the alcohol and the amount of caustic potash required for neutralization subtracted from the reading for the sample. The blanks did not require more than 0.1 cc. potassium hydrate for neutralization.

The end point taken was that obtained when the pink color persisted after vigorous shaking. The acid number calculated from the burette readings was the number of milligrams of potassium hydrate required to neutralize the acids present in 1 gram of the sample.

Saponification No.—Approximately $1\frac{1}{2}$ grams of oil were weighed into an eight-ounce oil bottle, the oil being accurately weighed on a chemical balance, using the pycnometer used in the determination of density as a weighing bottle. Duplicate samples were weighed out in each case. 20 cc. alcoholic potash were added and the mixture heated on a water bath at 80°C ., from 30 to 40 minutes. The samples were thoroughly shaken several times while saponification was going on. After cooling, the mixture was titrated with $N/2$ hydrochloric acid, using phenolphthalein as an indicator. Two blanks of 20 cc. each of alcoholic potash were run through with the samples each time and the mean of the results used in calculating the potash used in the saponification. The alcoholic potash solution was made up with 30 grams KOH dissolved in a small amount of water, and made up to 1 liter with 95 per cent. ethyl alcohol, and allowed to stand over night. The saponification No. calculated from the burette readings was the number of milligrams of caustic potash required to saponify one gram of the sample.

Specific Gravity.—Specific gravity determinations were made in all cases with the commonly used form of pycnometer, holding in each case between 25 and 30 cc. of oil. All determinations were made at 21°C . within a degree on each side.

Flash Test.—An open iron cup was used in making this test. The cup held 75 cc. of oil and was filled to within $\frac{3}{8}$ " of the top of the cup. The oil was heated at the rate of 3°C . per minute, over a Bunsen burner.

Fire Test.—The fire test was taken at that temperature at which the oil first began to burn continuously upon application of the small flame. Both flash and fire tests are recorded in degrees centigrade.

Viscosity.—The viscosity was measured in a standard Tagliabue instrument. Readings were made at 21°C ., and the temperature of the oil kept in all cases to within $\frac{1}{2}^{\circ}\text{C}$. on a side. The figure for viscosity given is that obtained from the number of seconds required for 70 cc. of the oil to run out multiplied by two, this being the amount of oil and the standard method of calculating recommended by the makers. 70 cc. of distilled water ran through this instrument in 23 seconds, at a temperature of 70°F ., making the viscosity of water at this temperature 46, with this instrument and method. The temperatures were regulated by pouring warmer or colder water into the jacket surrounding the instrument. All figures given

are the mean of two different readings made on the same sample.

Maumene Test.—Fifty grams of the sample were weighed into a No. 3 beaker which was placed inside a No. 4 beaker. The larger beaker was prepared by filling the space between the two beakers with a mixture of plaster of Paris and asbestos. After drying, the inside beaker may be removed and replaced by another of the same size. Since many of the samples tested frothed badly, particularly the cottonseed oil and linseed oil mixtures, a much higher form of beaker was used in these cases. Ten cc. sulphuric acid were added to the oil from a burette, during one minute. Stirring was effected by using a simple device, the object being to use the same conditions of stirring as possible during all of the tests. Instead of noting only the maximum temperature reached by the thermometer, we read the temperature each half minute until the thermometer showed a falling temperature. In this way we were certain of the actual maximum rise of temperature in all cases, and were able to observe some interesting facts with reference to the development of heat, by the mixture. The Maumene test is the maximum temperature rise obtained, subtracting from the thermometer reading the temperature of the oil and acid, which was kept at the temperature of the room. In some cases we found that a higher temperature rise may be obtained if the stirring is discontinued after the oil and acid are mixed. We attempted to use in all cases that condition of stirring which would give the maximum temperature rise.

DISCUSSION OF RESULTS.

Acid No.—The acid No. was determined on these mixtures of oils principally as a check upon the composition of the samples. They have not been made in a few mixtures, since some of the oil mixtures contain practically no free acids. These tests bring out the fact that the acid number is accurately determined by the method shown for all combinations of oil, whether they contain large amounts or small amounts of free acids.

Saponification No.—These tests were carried out in order to determine principally whether the saponification of a small amount of saponifiable oil is completely effected under the ordinary conditions of the test, when a large amount of unsaponifiable oil is present. The tests indicate that such is the case, and that the saponification number is readily obtained in all sorts of mixtures.

Gravity.—Specific gravity determinations were made as a further check upon the composition of the sample. Since the samples were made up by weight, and not by volume, it would not be expected that the curve showing gravity plotted against composition by weight would be strictly a straight line, although it plots nearly as a straight line, since the density of the oils were nearly unity. This is a simple illustration of the fact that additive relationships may not be found in some cases from purely algebraic reasons.

Flash Test.—The results on flash tests show very clearly that this phenomenon is not necessarily an

additive one. In those cases where there is any great difference between the flash points of the constituent oils, a very considerable curvature is to be found. In the cottonseed-linseed, and cottonseed-castor oil mixtures, where the flash tests of the constituent oils are nearly the same, the curvature is not apparent, and if it exists, lies within the range of observational errors.

Fire Test.—These results have not been plotted, but are similar to those obtained from the flash test.

Viscosity.—The curves of viscosity show considerable deviations from the additive relationship. We obtained indeed such curves even in these cases where the viscosity of the constituent oils is nearly the same. Nor do we obtain straight lines when we plot fluidity against composition. We believe those results are of interest, as an indication of the fact that neither the viscosity nor the fluidity of such solutions are necessarily additive, even though there is no evidence to indicate that either chemical or molecular compounds are formed.

Maumene Test.—Our results on Maumene tests indicate, on the whole, that the results are not additive, but that in mixtures containing a high Maumene test oil and a low Maumene test oil, that the results are greater than calculated from the law of averages at the upper end of the curve and lower than that calculated from the law of averages at the lower end of the curve. In no case were we able to duplicate the Maumene test on any given mixture within a degree, or even within several degrees, when tests were made time after time, or day after day, upon the same sample. We have tried to use every possible precaution with reference to duplicating the conditions of the test time after time, but we have found this test to give most unsatisfactory results, and we consider it almost useless as a quantitative method.

Of the different factors which determine the rise in temperature of a mixture of oil and sulphuric acid, there seems to be quite a few which are beyond the control of the operator, and the result is that the different samples of the same oil mixture will give temperature rises that differ between themselves as much as 5° and even 10° centigrade.

We have found that the rate of stirring has an important influence upon the result, and our experience has been that a method of stirring must be used which differs with different mixtures, in order to get the highest temperature rise.

This seems to be due to the fact that the stirring has two different effects: it tends to mix the oils intimately with the acid, and it also assists in the cooling of the mixture. Consequently, after stirring has mixed the oil and the acid thoroughly, further stirring only assists in the loss of heat by the mixture. This carries with it, of course, the assumption that the oil and acid stay mixed.

The more viscous the oil the greater the tendency to stay mixed. Oils containing castor oil do not require more than a certain amount of stirring. Mixtures containing a large amount of oils of low viscosity require constant stirring in order to keep the acid in contact with the oil.

There are other important factors, however, which influence the development of heat in a mixture of oils and sulphuric acid. The reaction appears to be a function of the temperature itself, which is in its turn a function of the velocity of the reaction. Any condition which influences the initial velocity of the reaction, therefore, has an influence upon the quantity which is under observation, which is the maximum temperature rise.

If the reaction starts off briskly the total rise will be correspondingly higher than is the case where, for some reason, the velocity of the reaction is slower at the beginning.

We think it probable that it is this dependence of the quantity of the reaction upon its own velocity that interferes so seriously with its yielding results which may be duplicated within satisfactory limits.

SUMMARY OF RESULTS.

Certain tests commonly used in oil analysis (the viscosity, flash test, fire test and Maumene test) have been shown to follow a law of mixtures which is not an additive one, and hence if interpolations are made from the data obtained from such tests, the results will be in error, to a very considerable amount, in some cases.

These results call attention to the possibility of many other physical tests being non-additive. They also suggest the possibility that certain chemical tests, in which a complete chemical reaction does not occur, may not be additive.

The saponification No. is shown to be an additive relationship even for small percentages of one oil in presence of another.

The Maumene test as carried out at the present time is incapable of yielding results which can be used in making a quantitative analysis by the interpolation method.

Work is being done at the present time upon the iodine Nos. of these oil mixtures.

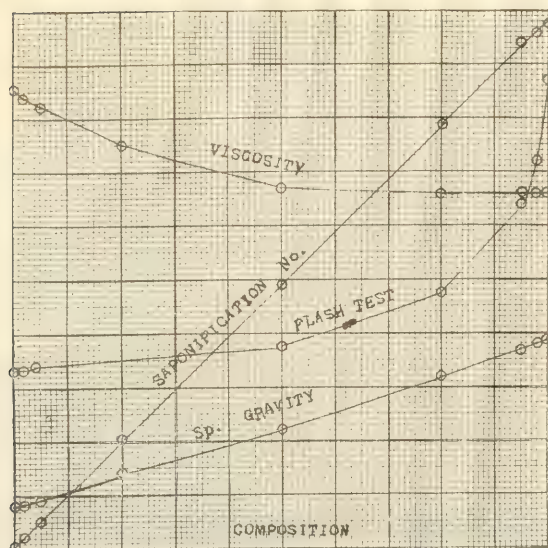
NOTES ON THE TABULATED RESULTS AND CURVES.

The tabulated results show the figures obtained on all of the tests made.

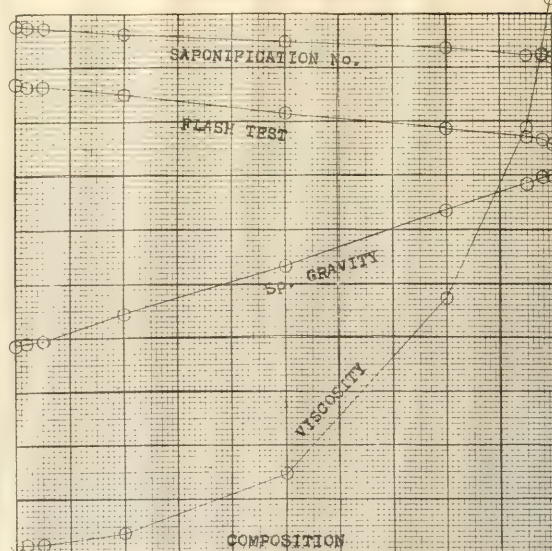
In the case of some of the mineral oil-castor oil mixtures the constituent oils are not soluble in one another at ordinary temperatures. These mixtures were analyzed, however, together with the rest of the samples, the mixture being very thoroughly shaken before the sample for the test was taken out of the bottle. These mixtures are marked in the tables with a star.

The viscosity, saponification No., flash test and specific gravity have been plotted in the curves. Observational points are shown by small circles. In the case of the saponification Nos. the diameter of this circle indicates a difference of saponification No. of 4; in the case of specific gravity the diameter of the circle indicates a difference of specific gravity of 0.0020; in the case of the flash tests the diameter of the circle indicates a difference of temperature of 4° C. In the case of viscosity the diameter of the circle indicates a difference of 4 when castor oil is absent and a difference of 40 when castor oil is present.

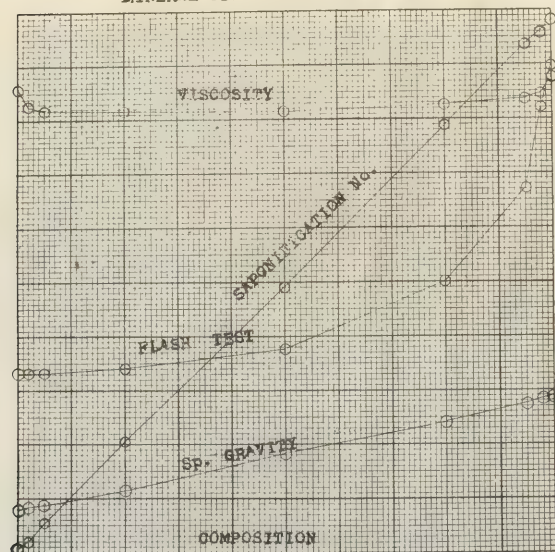
MINERAL OIL-LINSEED OIL



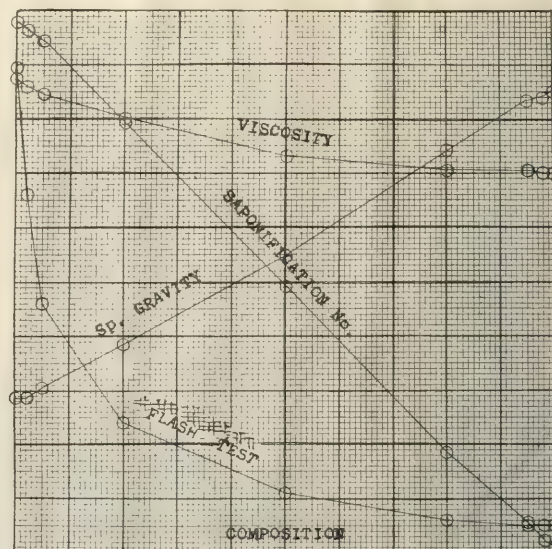
LINSEED OIL-CASTOR OIL



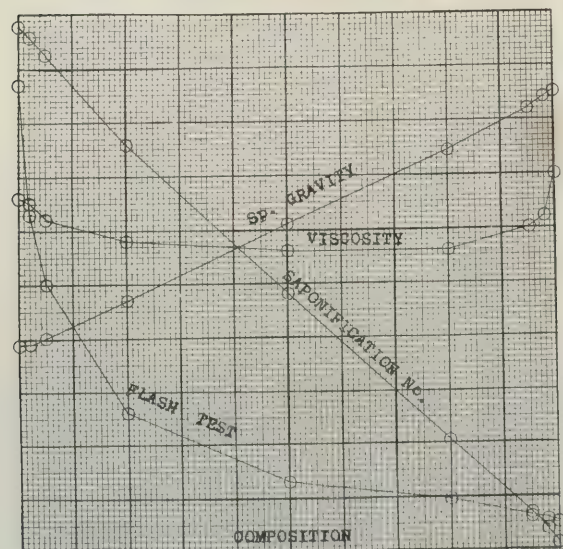
MINERAL OIL-COTTONSEED OIL



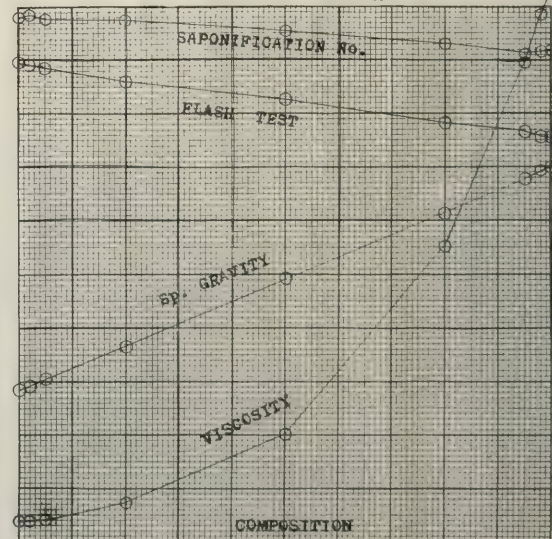
COTTONSEED OIL-ROSEIN OIL



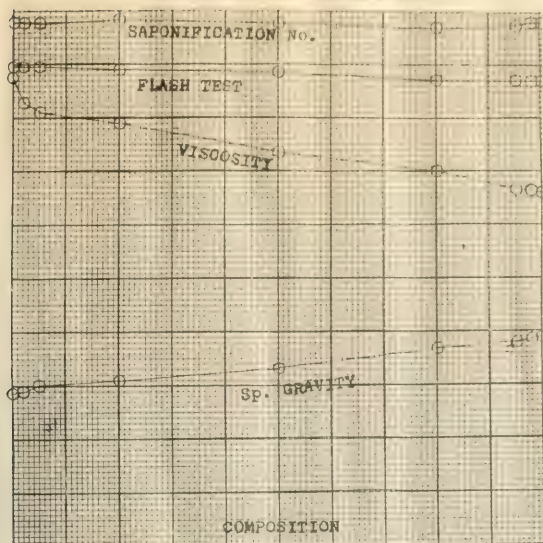
LINSEED OIL-ROSEIN OIL



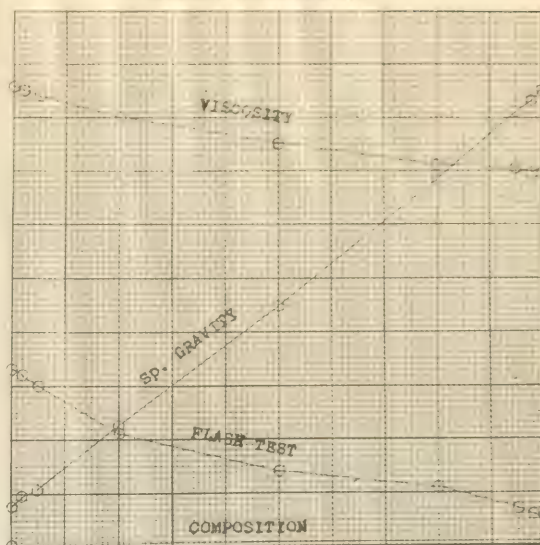
COTTONSEED OIL-CASTOR OIL



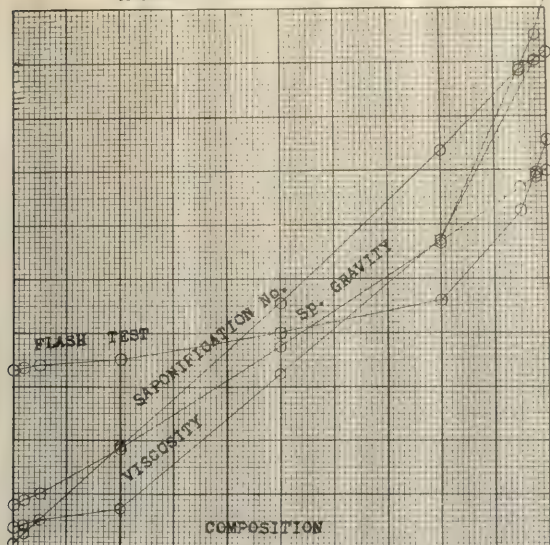
COTTONSEED OIL-LINSEED OIL



MINERAL OIL-ROsin OIL



MINERAL OIL-CASTOR OIL



MINERAL OIL-COTTONSEED OIL.

Lab. No.	Per cent mineral	Per cent cottonseed	Specific gravity	Acid No.	Sap. No.	Flash test	Fire test	Manné No.	Vis. 70° F.
4921	100	0	0.8977	0.03	1.0	186	217	6.2	171.6
4990	98	2	0.8981	..	3.6	186	208	8	164.8
4989	95	5	0.8986	..	10.5	186	210	11	163.6
4988	80	20	0.9016	..	40.6	188	213	25	163.2
4987	50	50	0.9084	0.06	98	195	225	50.6	162.6
4986	20	80	0.9140	..	156.8	220	257	63.5	165
4985	5	95	0.9173	..	187.3	254	330	63	167
4984	2	98	0.9183	0.08	191.4	284	338	68	169
4983	0	100	0.9184	0.08	196.1	299	340	71	175

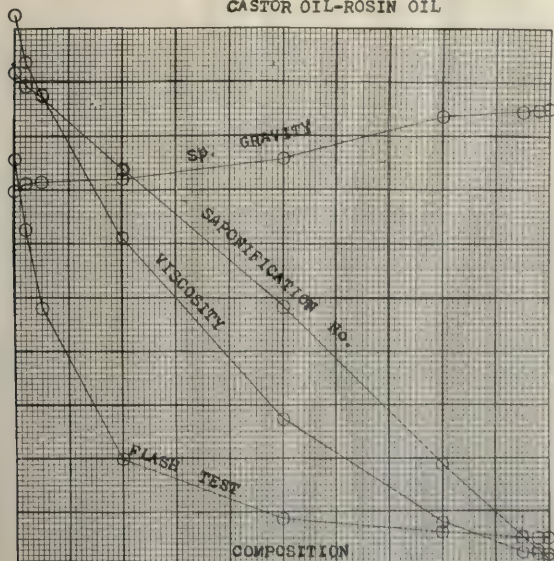
MINERAL OIL-LINSEED OIL.

Lab. No.	Per cent mineral	Per cent linseed	Gravity	Acid No.	Sap. No.	Flash test	Fire test	Manné No.	Vis. 70° F.
4921	100	0	0.8977	0.03	1.0	186	217	6.2	171.6
4935	98	2	0.8983	0.06	4.3	186	219	9.8	168
4934	95	5	0.8992	0.06	8.7	188	221	12.2	162
4933	80	20	0.9041	0.25	40.8	192	225	35.5	149
4932	50	50	0.9119	0.64	96.5	195	229	64	136
4931	20	80	0.9221	1.00	158.2	215	243	82	132.2
4930	5	95	0.9262	1.22	189.1	249	310	91	132
4929	2	98	0.9281	1.28	191.8	264	326	92	132
4810	0	100	0.9286	1.30	195.7	294	334	101	132

MINERAL OIL-CASTOR OIL.

Lab. No.	Per cent mineral	Per cent castor	Gravity	Acid No.	Sap. No.	Flash test	Fire test	Manné No.	Vis. 70° F.
4921	100	0	0.8977	0.03	1.0	186	217	6.2	171.6
4920	98	2	0.8987	0.06	4.9	187	219	9.5	180
4919	95	5	0.9000	0.11	10.1	188	220	12	190
4918	80	20	0.9082	0.56	37.5	190	223	27	244
4917	50	50	0.9273	1.25	90.3	200	228	49.5	745
4916	20	80	0.9465	2.28	147.3	212	257	51.5	1240
4915	5	95	0.9569	2.66	176.8	245	303	58.5	1880
4914	2	98	0.9587	2.72	180.1	259	304	51	2000
4802	0	100	0.9599	2.86	183.5	271	304	58	2146

CASTOR OIL-ROsin OIL



MINERAL OIL-ROsin OIL.

Lab. No.	Per cent. mineral.	Per cent. rosin.	Gravity.	Acid No.	Sap. No.	Flash test.	Fire test.	Maumené No.	Vis. 70° F.
4921	100	0	0.8977	0.03	1.0	186	217	6.2	171.6
4928	98	2	0.8996	184	217	7.5	170
4927	95	5	0.9006	180	210	7.1	168
4926	80	20	0.9125	162	196	9.8	160
4925	50	50	0.9347	148	185	17	150
4924	20	80	0.9586	142	177	18	142
4923	5	95	0.9712	134	162	21	140.8
4922	2	98	0.9731	132	159	21.8	139.8
4818	0	100	0.9750	0.00	2.0	130	158	20	139.6

LINSEED OIL-CASTOR OIL.

Lab. No.	Per cent. linseed.	Per cent. castor.	Gravity.	Acid No.	Sap. No.	Flash test.	Fire test.	Maumené No.	Vis. 70° F.
4810	100	0	0.9286	1.30	195.68	294	334	101	132
4809	98	2	0.9290	1.30	194.90	293	334	98	134
4808	95	5	0.9294	1.30	194.40	293	334	100	136
4807	80	20	0.9344	1.58	192.18	290	329	92	178
4806	50	50	0.9432	1.86	189.72	283	320	91	393
4805	20	80	0.9534	2.36	187.20	277	316	73.5	1043
4804	5	95	0.9583	2.78	184.09	274	311	73.5	1677
4803	2	98	0.9597	2.78	185.50	273	306	47	1946
4802	0	100	0.9599	2.86	183.52	271	304	58	2146

COTTONSEED OIL-LINSEED OIL.

Lab. No.	Per cent. cotton-seed.	Per cent. linseed.	Gravity.	Acid No.	Sap. No.	Flash test.	Fire test.	Maumené No.	Vis. 70° F.
4983	100	0	0.9184	0.08	196.1	299	340	71	175
4998	98	2	0.9188	0.08	196.0	299	340	69	165.6
4999	95	5	0.9201	0.11	195.0	299	340	74.5	162
5000	80	20	0.9209	0.31	197.2	298	340	79	158.4
5001	50	50	0.9232	0.64	194.4	297	340	77.5	146.4
5002	20	80	0.9268	0.98	193.9	294	336	97.5	140
5003	5	95	0.9280	1.12	194.7	294	337	102	132.6
5004	2	98	0.9284	1.15	196.2	294	336	105	132
4810	0	100	0.9286	1.30	195.7	294	334	101	132

LINSEED OIL-ROsin OIL.

Lab. No.	Per cent. linseed.	Per cent. rosin.	Gravity.	Acid No.	Sap. No.	Flash test.	Fire test.	Maumené No.	Vis. 70° F.
4810	100	0	0.9286	1.30	195.7	294	334	101	132
4825	98	2	0.9290	1.14	190.8	246	334	102	130
4824	95	5	0.9301	1.14	184.7	220	322	93.5	124
4823	80	20	0.9370	0.92	151.7	172	215	84	116
4822	50	50	0.9510	0.58	96.0	146	172	86	112
4821	20	80	0.9644	0.19	40.8	139	160	52.5	112
4820	5	95	0.9720	0.03	13.6	132	162	31	120
4819	2	98	0.9741	0.00	7.7	131	159	26	124
4818	0	100	0.9750	0.00	2.0	130	158	20	139.6

CASTOR OIL-ROsin OIL.

Lab. No.	Per cent. castor oil.	Per cent. rosin.	Specific gravity.	Acid No.	Sap. No.	Flash test.	Fire test.	Maumené No.	Vis. 70° F.
4802	100	0	0.9599	2.86	183.52	271	304	58	2146
4811	98	2	0.9611	2.86	178.82	245	314	56	1977
4812	95	5	0.9613	2.69	175.26	216	285	54	1855
4813	80	20	0.9620	2.36	147.57	160	215	56	1320
4814	50	50	0.9658	1.64	96.37	137	180	57.5	647
4815	20	80	0.9736	0.61	37.53	132	165	39.5	259
4816	5	95	0.9744	0.14	10.37	130	162	27	142
4817	2	98	0.9748	0.08	5.23	130	162	21	140
4818	0	100	0.9750	0.00	2.0	130	158	20	139.6

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A COMPARISON OF METHODS OF DETERMINING UNSAPONIFIABLE MATTER IN WOOL OILS.

By AUGUSTUS H. GILL AND A. E. SHIPPEE.

Received December 23, 1910.

There are two methods in common use for determining unsaponifiable matter in wool oils, the usual extraction method with gasoline, and the method by difference. In the latter method the free acid is determined, then the combined fatty acids, these latter calculated as olein, added to the free acid, and this sum subtracted from 100, giving the unsaponifiable matter. As this method is more rapid, and is quite extensively used, it seemed advisable to compare it with the other.

Procedure: Extraction Method.—The free fatty acids, unsaponifiable matter and saponification number were determined according to the procedure given in Gill's "Oil Analysis."

COTTONSEED OIL-ROsin OIL.

Lab. No.	Per cent. cotton-seed.	Per cent. rosin.	Gravity.	Acid No.	Sap. No.	Flash test.	Fire test.	Maumené No.	Vis. 70° F.
4983	100	0	0.9184	0.08	196.1	299	340	71	175
5005	98	2	0.9186	0.08	192.7	252	338	69.8	172
5006	95	5	0.9205	0.08	188.8	212	315	69.5	169
5007	80	20	0.9284	0.03	158.1	168	205	67.5	160
5008	50	50	0.9447	0.03	98.0	142	165	58.5	146
5009	20	80	0.9641	0.00	366	132	150	45.5	140.8
5010	5	95	0.9731	0.00	11.6	130	145	35.5	141
5011	2	98	0.9739	0.00	4.3	130	143	27.5	140
4818	0	100	0.9750	0.00	2.0	130	148	20	139.6

Procedure: Differential Method.—Ten grams of the oil are weighed into a 250 cc. Erlenmeyer flask, dissolved in neutral alcohol, heated to 65–70°, and titrated with *N*/6 alcoholic potash, using phenolphthalein as an indicator. This operation gives the free fatty acids. From this point two processes are available: (1) To the solution of soap and neutral fat is added 25 cc. of *N*/2 alcoholic potash, the solution boiled, 100 cc. of water added and the boiling continued. Finally the excess of alcoholic potash was titrated for with hydrochloric acid. The sum of these two figured as oleic acid and the triglyceride of oleic acid, respectively, gives the saponifiable matter. The unsaponifiable matter is the difference in weight between the sample taken and this amount. (2) After titrating for the free acids, an excess of alcoholic potash is added and the solution boiled. When saponification was complete, the alcohol was removed by adding 600 cc. of water and boiling, water being added as it evaporates. The fatty acids were then precipitated with dilute sulphuric acid. The boiling was continued till the fatty acids formed a clear liquid on top of the aqueous solution. They were then separated in a separatory funnel and washed till the washings were free from mineral acid. The fatty acids were then dissolved in neutral alcohol, heated to 65–70°, and titrated with *N*/2 alcoholic potash. The difference between this result and the free acid figured as the triglyceride of oleic acid and the free acid figured as oleic acid in the saponifiable matter; the difference between the sum of the free acid and saponifiable matter and the weight of oil taken is the unsaponifiable matter.

The extraction method suffers from the disadvantage of incomplete extraction by gasoline, of the solubility of soap therein, from the difficulty of complete removal of the solvent used in extracting the oil, and of losing any volatile constituents of the unsaponifiable matter.

The errors in the differential method come from assuming that all the acids and neutral fats consist of oleic acid and its triglyceride, and in the second modification from a loss of fatty acids in manipulation and their solubility in hot water.

From this it would seem that the method of finding the unsaponifiable matter by difference is sufficiently accurate for industrial purposes and is to be preferred to others on account of the greater rapidity and ease of manipulation.

The following table shows the results obtained by the two methods: the average difference between the two methods is less than the difference between two determinations by the same method, except with oil No. 3.

Description of oil.	Sp. gr. 15.5° C.	Unsapon. Matter by ext.	Sapon. Matter by diff.	Sap. value	Per cent. free acid as oleic.
Scotch wool.....	0.908	65.7	65.4	73	12.8
Wool oil.....	0.908	91.7	90.9	17	3.3
Oleine, 42 per cent. sapon.	0.911	58.5	56.6	88	41.3
Eng. oleine, 42 per cent. sapon.....	0.911	59.4	59.2	80	40.7
Woololeine, 75 per cent. sapon.....	0.910	31.2	31.0	140	65.2
Woololeine, 35 per cent. sapon.....	0.910	65.2	65.3	69	32.6

ON THE LIABILITY OF WOOL OILS TO GUM ON OXIDATION.

By AUGUST S. H. GILL and A. J. SHIPPEE.

Received December 23, 1900.

Besides the determination of the amount of unsaponifiable matter, free acid, and the flash point of wool oils, it is desirable to know if they gum on exposure to the air. An excellent opportunity for this is offered by their exposure on the textile fibers in the course of manufacture.

Richardson and Hanson¹ have used an apparatus in which a current of air was drawn over the hot oil. Although primarily designed for cylinder oils it gives useful information with wool oils. The apparatus consists of a copper oven 10" x 10" x 7", all joints brazed, which constitutes the oil or water jacket. This jacket surrounds a chamber 5" x 7" x 1" in height. The tray measures 4" x 6½" x 1½" deep. The inner chamber is surrounded by half-inch copper tube in eight coils; the last coil enters the chamber at the back of one corner and the exit is at the opposite corner diagonally and is connected with a half-inch copper exit tube, which is connected with a suction pump. The air is measured by a meter joined to the first coil of copper pipe surrounding the chamber, so that the meter is at the room temperature. A tube leads from the center of the chamber to the outside, and is fitted with a thermometer. The chamber is closed by an asbestos board outside of which is a copper plate, held firmly over the mouth of the chamber by two thumb-screws. Procedure: ten cc. of the oil are placed in the chamber in a shallow pan 4" x 6½" x 1½". Air at 100° is drawn over the oil at the rate of from 3 to 5 cubic feet in four hours, which was the length of a run. The tendency of an oil to oxidize and gum is indicated by its increase in viscosity.

The pans first tried were made of tinned iron. These were unsatisfactory because the metal was so thin that a level surface could not be obtained and consequently the oil did not cover the bottom of them in an even film. By using a pan made of iron about 1/16" thick which had a level, rigid bottom, this difficulty was removed. The machine was leveled by placing 10 cc. of oil in it and, after allowing it to stand for an hour, noting at what point the bottom was not covered by oil. After one or two trials the apparatus could be adjusted so that every part of the bottom was covered with a layer of oil. Since there are 168 sq. cm. area, 10 cc. would form a layer 0.06 cm. thick; therefore, the apparatus was considered level enough when this condition was reached. In order that the pan might be placed in the same position each time, a mark was made on one corner and it was placed against two sides of the chamber, always having the marked corner opposite to the one touching the sides.

In order to test the viscosity after oxidation a special form of apparatus was necessary, the amount of oil oxidized being far too small for the ordinary forms. The only method which seemed feasible was that of allowing the oil to flow through an orifice. A tube

¹ *J. Soc. Chem. Ind.*, **24**, 315 (1905).

was tried, surrounded by water at 100°, having a capillary sufficiently large to allow a stream to flow. This was unsuccessful because, when the oil became more viscous after oxidation, the stream would change to a drip and this would spoil the determination. If the size of the orifice were increased sufficiently to allow a stream of the more viscous oil to flow, the less viscous oil would run out so fast that the time could not be taken with accuracy. It was necessary, therefore, to depend upon a drip entirely and use a lower temperature.

The apparatus, which was finally used for testing the viscosity and which gave very satisfactory results, consisted of a glass tube about 80 cm. long and 3 mm. in diameter placed in an ordinary condenser jacket. The lower end of this was reduced to a capillary by placing it in the flame of a Bunsen burner and slowly turning, allowing the edges to run in towards the center. It was found that in this way a very smooth, round capillary of any size desired could be made, the size used being approximately 0.3 mm. in diameter. Two marks 25 cm. apart were made on this tube by placing narrow strips of pressure tubing on it, the lower mark being placed 25 cm. from the capillary. A temperature of 25° C. was maintained by a water bath circulated through the condenser by means of a circulating pump. The tube was filled to a point 10 cm. above the upper mark by placing a piece of rubber tubing on the upper end of it which projects above the condenser jacket and drawing the oil up through the capillary by suction. The time required for the oil between the two marks to run out was taken by a stop-watch. For the first two or three trials this varies slightly but finally reaches a constant value which can be checked to two-fifths of a second. This apparatus could be standardized against water or olive oil, but, since only the increase in viscosity is desired, this is not necessary.

By lengthening the time or increasing the temperature, the difference in viscosity can be increased. It was found, however, that when the differences in viscosity were much greater than those obtained, the results were very unsatisfactory, for the reason that the change in the time required for the given volume to flow out through the capillary was out of all proportion to the increase in viscosity. In such a case, the oil would run out comparatively fast at the beginning but would suddenly slow down and in many cases stop entirely; the results would vary from one or two seconds to any value whatever.

The table shows that the increase in viscosity is greatest when the oil contains the greatest amount of saponifiable matter. It is not, however, proportional to the amount of saponifiable matter present. In oils No. 1 and No. 6 which contain approximately the same amount of saponifiable matter, the difference in the change of viscosity is 14.3 per cent. In oils No. 3 and No. 4, which also contain about the same amount of saponifiable matter, the difference in the change of viscosity is 7.8 per cent. In both these cases the oil which has the higher iodine number has the greater increase in viscosity, thus

indicating that oils containing more of an unsaturated constituent would be more liable to oxidize, which is in accordance with the fact. It is possible that the conditions under which these experiments were carried out were such that only the unsaturated parts of the oils were oxidized, the unsaponifiable part remaining unchanged. If this were the case, it would be necessary to get a greater increase in viscosity by raising the temperature or lengthening the time, which would require a different method of measuring the viscosity.

The results obtained are shown in the table below, the oils used being the same as those in the preceding paper.

Description of oil.	Viscosity in seconds before heating.	Viscosity in seconds after heating.	Per cent. increase of viscosity.	Iodine number.	Unsaponifiable matter.	Free acid.	Flash, °F.
Scotch wool.....	12.0	16.2	35.0	38	65.5	12.8	306
Wool oil.....	14.4	15.0	4.2	27	91.0	3.3	340
Oleine, 42 per cent. sap	17.2	24.8	44.2	58	57.5	41.3	325
Eng. oleine, 42 per cent. sap.....	19.2	26.2	36.4	51	59.3	40.7	335
Wool oleine, 75 per cent. sap.....	13.4	24.6	83.5	140	31.1	65.2	346
Wool oleine, 35 per cent. sap.....	14.4	21.6	49.3	46	65.3	32.6	327

The first and last oils contain the same amount of saponifiable matter; this is 12.8 per cent. free acid in the first oil, and nearly all free oleic acid (31 per cent.) in the last oil; the change in viscosity is 35 per cent. in the first oil and 49 in the last. It would seem that the change is not wholly due to the free oleic acid and that the first oil is to be preferred. A similar condition prevails with oils Nos. 3 and 4, except the fatty acid contents are practically the same; No. 4 shows 7 per cent. less viscosity after heating, and is to be preferred on this account.

It is worthy of notice in this connection that the iodine number gives information of almost identically the same value, hence it would seem that it might be said, in selecting a wool oil, other things being equal, particularly the free acid and unsaponifiable matter, choose that one having the lowest iodine value.

The flash points were taken as an additional criterion.

THE EXACT ELECTROLYTIC ASSAY OF REFINED COPPER. 1. STANDARD METHOD. 2. RAPID ASSAY BY ROTATION OF THE ELECTROLYTE IN A SOLENOID.

By GEORGE L. HEATH.

Received December 20, 1910.

Prof. F. C. Frary¹ has described an apparatus which assures a very rapid deposition of metals by surrounding the beaker with a coil of insulated copper magnet wire through which a current is passed, making about 500 turns, and thus producing a magnetic field within the solution.

The lines of force passing from anode to cathode are constantly diverted in one direction by the pull

¹ *J. Am. Chem. Soc.*, 17, 395; *Z. Elektrochem.*, 23, 358.

of the outside current, causing a rapid rotation of the solution itself.

This discovery was given to the writer by Mr. Zimmerschied, of Michigan University, and before the appearance of Prof. Frary's notable paper. We constructed rotary devices, and the data to be recorded show our standard slow method which has been adopted, since 1897,¹ in several large plants together with the development of the solenoid with the aid of the author's assistants and the experience of Mr. W. H. Bassett and assistants, of the American Brass Co., as communicated by him.

Discussion of the Theory.—The prior discovery was made by the latter that copper, containing as high as 0.1 per cent. of arsenic, would give a pure deposit in a very short time with the rotary device, in the special acid "stock" mixture devised by us for the standard assay of 5 grams of refined metal.

The principle has been extended, by the writer and assistants, to the deposition of pure copper in the presence of 0.5 per cent. of arsenic, and even to the assay of 3 grams of Whitneyite, containing 10 per cent. of arsenic.

We have, since that time, perfected the slow assay with stationary electrodes, so that copper containing as high as 0.5 per cent. arsenic can be properly deposited by the electric current in about 16 hours from a 3.5- to 5-gram sample, provided that no more than a trace of antimony is present and the acid stock solution is increased one-half, or more, to hold back the impurities.

In the case of such impure material, it is advisable, in order to be sure that the deposit is strictly pure, to dissolve the cathode copper by placing the plate in a tightly covered beaker in a fresh lot of diluted acid mixture, and to redeposit the copper on the same cathode, and reweigh it.

Recently, Mr. W. C. Ferguson,² of the Nichols Copper Co., has given an excellent method for the assay of blister and converter material, in which the operator is directed to take a large quantity (80 grams, or more) in order to eliminate errors of sampling such material, and to dissolve and divide this sample volumetrically, checking each set of assays against a blank assay of analyzed refined metal, run at the same time, instead of making a chemical test for the completion of the electrodeposition.

This paper is, however, written, primarily, on the analysis of refined metal, for which a more exact method of getting the weights and estimating the end-point is considered necessary.

The advantage of the solenoid over any mechanical device for the rotation of electrodes³ is due to the prevention of loss by the spraying from the anode, as the beaker can be covered with a double pair of split watch-glasses. The arsenic is held back, the moderate heat of the coil assists deposition, and the temperature can be controlled by changing the size of wire, and by introducing a water circulation between

the beaker and copper cylinder. Results obtained with the rotary device average from 0.003 per cent. to 0.01 per cent. higher than with the 16-hour assay of refined metal (averaging 0.007 per cent. on pure copper), and this is due to a trace of platinum which is carried over from the anode, under the influence of heat, *nascent nitrous acid*, and high current.

If the cathode is dissolved in very dilute acids, the Pt may be filtered out, weighed and deducted from the total deposit.

The explanation of the remarkable purity of the cathode deposit may be found in the fact that the solution becomes pretty warm and more oxidizing, and that the time is too short to permit the reduction of much nitric acid to ammonia, the solution after removal of copper having been found to be much more acid when the metal has been rapidly deposited with high current in the rotary solenoid and on gauze cathodes.

SAMPLING.

This procedure varies with the conditions in different works, but it is easy to get a good sample of a casting of refined metal by drilling properly spaced holes half way through from top, side and bottom, having first started the holes with a little larger drill, just enough to remove the surface oxide.

If the metal is very pure it is not necessary to drill so deep, not over $\frac{1}{2}$ " to 1 inch.

The drillings are cleaned from any trace of dust, tested with a magnet, and tightly bottled.

From this, two samples of 5 grams can be taken with a spatula that will check within 0.01 per cent.

1. *Details of Standard Slow Method.*—A 5-gram sample has been adopted by ourselves and at several other plants, because it eliminates errors of sampling the bottled drillings in the case of refined metal, and is the largest amount of material which can be started at close of business and taken off and weighed the next day before dinner-time without oxidation from too large a current.

Assays must finish, under the conditions described, in 16 to 18 hours, and *without any* more than a trace of preliminary gassing at the cathode, or be rejected.

This theorem goes farther than the requirement of other laboratories, but has been proved that we can thus absolutely prevent an occasional oxidation, or absorption of hydrogen, which can not be detected by any marked change in color, but which may amount to 0.02 per cent. by weight.

The assays are started with a current whose normal density, counting both sides of the cathode, is 1 ampere per 100 sq. cm., and in the morning as soon as the liquid is colorless, the split watch-glasses, covering the beaker, are washed down with a fine jet, and the current reduced to 0.5 ampere. If assays have to go more than 18 hours and the cathode shows bubbles of gas, the current is cut to 0.25 ampere to avoid oxidation or hydrogen absorption.

The sample is weighed into a lipless beaker, about $\frac{7}{8}$ inches high, and $2\frac{1}{4}$ inches in diameter outside, across the bottom, and of 300 cc. capacity, which can be obtained from Eimer & Amend, New York.

¹ *Trans. A. I. M. E.*, **27**, 390 (1897). *J. Am. Chem. Soc.*, **26**, 1120 (1904).

² *THIS JOURNAL*, **2**, 187 (1910).

³ *Eng. and Min. J.*, **89**, 89 (1910).

In the slow method, chemists use the foil, plain or corrugated. The cylinder is 2 inches (or 5 cm.) high and the closed cylinder has a total surface of 150 sq. cm. The cylinder, opened on one side, which the writer prefers for the ease and quickness with which it may be withdrawn from the solution and dropped into a beaker of water, is 100 sq. cm., counting both sides and the stem extends 12.5 cm. above the cylinder.

The sample of drillings is heated on a steam plate, just below the boiling point, with a mixture of exactly 7 cc. of c. p. nitric acid (sp. gr. 1.42), 10 cc. of sulphuric acid (sp. gr. 1.84), and 25 cc. of distilled water, with the beaker tightly covered until solution is complete, as can best be determined by holding the beaker over a white paper.

The solution is brought to a total volume of 120 cc. before electrolysis. When the deposition is thought to be complete, 1 cc. of liquid is withdrawn with a glass medicine dropper, placed in the cavity of a white porcelain tile, and treated with a few drops of freshly prepared hydrogen sulphide water.

Any copper over 0.00005 gram will show at once, and is easily distinguished from the yellow of arsenic which would show later.

After years of experiment, we have found that the proportion of acids given produces exactly the right equilibrium of the acid ions in the solution at the completion of the assay, preventing the deposition of the arsenic if the amount of total acid is increased with the arsenic.

In practice, some works, like ourselves, make up a dilute acid, mixed, "Stock Solution" and run it from a large burette.

For 5 grams metal, containing less than 0.03 per cent. arsenic, the "Stock Solution" required would be 40 cc.; 0.03 per cent. to 0.100 per cent. arsenic, 50 cc.; for 0.11 per cent. to 0.500 per cent. arsenic, 60 cc.

It is found to facilitate the instantaneous removal and washing of the cathode without loss, if the beakers are arranged in a row under a vulcanite plate $\frac{1}{4}$ inch thick and perforated with one small hole for each wire stem to make connection with the split, brass terminals (which rest in pairs about $\frac{15}{16}$ inch apart from center to center) and are perfectly protected by the plate from acid fumes.

The under side of this strip, or shelf, is $12\frac{1}{2}$ inches from the table, and the beakers stand on double-headed, turned wooden spools, 6 inches high. When an assay is finished, the spool can be slipped aside, and with one motion the beaker can be lowered, and a beaker of distilled water raised to cover the electrode and remove acid before it is disconnected.

The cathode is then washed well with a jet, the water removed by pouring a lot of clear 94 per cent. alcohol over the plate, and the little that remains after draining a moment is then burned off and the plate carefully passed across the flame of the lamp to be sure that no trace of liquid remains between the stem and the cylinder.

The electrodes are cleaned, heated, and weighed

before use, allowing the same length of time for cooling before weighing, and the weights should be compared very carefully, and regularly, with a standard set.

The foregoing claims for the deposition of pure copper, either with the slow method or the "rotary," do not strictly apply to copper containing more than a trace of antimony, selenium or tellurium, in which special methods of preliminary purification of electrolyte are employed,¹ or a "dope" may sometimes be used as recommended by the chemists of one of the Tennessee copper companies.²

To relieve any doubt as to the purity of the copper deposits, in the case of material carrying over 0.1 per cent. arsenic, the cathode can be redissolved without loss by placing the cathode copper in 40 cc. of acid "Stock Solution" diluted to 120 cc. with water, allowing it to stand on the steam plate just below boiling for about an hour.

The beaker must be carefully covered with a glass cover, perforated near one edge with a small drilled hole just large enough to pass the stem of the electrode. If an assay was allowed to boil, any steam which raised the cover would cause a certain loss of copper solution by spraying.

Check results should agree within 0.01 per cent.

It will be noted that, whereas Mr. Ferguson recommends the previous removal of silver from converter metal when aliquot portions of a large sample are volumetrically taken, we find it better with standard refined metal to deposit the silver with the copper, and determine silver by a special assay if required, since weighing, even with the elaborate precautions sometimes adopted, is more accurate than measuring.

In the case of refined copper, we must also have an absolute test of the completion of the deposition, which is obtained by taking out 1 cc. of the electrolyte, when the assay is thought to be finished, by means of a glass medicine dropper, and treating it on a white porcelain tile with a few drops of freshly prepared water solution of hydrogen sulphide.

If the estimation of the arsenic is desired, the electrolyte from a 5- or a 10-gram assay can be used for the purpose, with certain precautions to be described in a paper on the estimation of the arsenic group.

Some works find the 110-volt direct lighting current to be the most satisfactory source of electric power, which is reduced by small rheostats, in series with each group of 5 or 6 assays, or by a bank of incandescent lamp sockets, into which lamps of different candle-power can be inserted to vary the current.

Where the current is alternating, recourse is had to small "motor-generator" sets, rectifiers, for the purpose of charging large storage batteries, which give a much steadier current than very small machines.

2. *Rapid Assay by the Rotation of the Electrolyte.*—Rotation in a magnetic field offers great possibilities for special rapid work where results are desired at once on copper or slags containing arsenic and antimony.

The principle has been somewhat discussed and so

¹ *Trans. A. I. M. E.*, **27**, 390 (1897); *J. Am. Chem. Soc.*, **26**, 1120 (1904).

² *Eng. and Min. J.*, **89** (1910).

should not be employed in the regular battery assay with small apparatus as the heat, if not too near the boiling point, is one factor in holding the arsenic in solution.

Rapid Assay of Copper in Furnace Slags.—Thorn Smith¹ and others have improved the methods of assay of reverberatory and waste cupola slags containing such a large amount of iron that the old ammonia precipitation (Heine's blue test) will not yield all the copper.

The rapid electrolysis by rotating anode² or by the solenoid is far preferable, and the latter device is the best of the two, as we use it.

Two and five-tenths grams of waste slag, or 1 to 2 grams of richer slag or ore, are weighed and placed in a No. 4 porcelain casserole, moistened and treated with 15 cc. of strong nitric acid and boiled one minute to decompose it, but not long enough to burn on the bottom.

Most slags decompose well if the slag has been chilled by granulating in water at the furnace. Then add 10 cc. of concentrated sulphuric acid and boil to dryness over a gauze, but stop just before the sulphuric acid begins to fume. This allows a trace of nitric acid to remain, and in presence of excess of iron produces a good deposit in the rotating solution in 30 minutes, with a current whose strength is N. density 100 sq. cm. = $4\frac{1}{2}$ amperes, counting both sides of the cathode.

The assay must be watched and split electrode of foil removed promptly.

The gauze cathode will not be necessary except for rich slags, requiring over 30 minutes. The residue in the casserole is treated with water while still hot, and washed directly into a regulation beaker, without filtration.

Chilled waste slags, which are low in iron oxide and high in lime, can sometimes be decomposed in a few minutes with a simple boiling in the tall beaker in 60 cc. of "Acid Stock Solution" and then transferred to the solenoid. Sometimes, as metallurgical chemists find out to their cost, special slags require an aqua regia treatment and fusion of the residue.

CALUMET AND HECLA SMELTING WORKS,
HUBBELL, MICHIGAN.

THE DETERMINATION OF ARSENIC AND ANTIMONY IN COPPER.

By GEORGE L. HEATH.

Received December 20, 1910.

This paper will summarize the principal methods employed in American foundries and refineries, and include a new rapid method for arsenical metal by direct titration of the electrolyte from battery assays or by titration of a solution of precipitated sulphides of the arsenic group.

The principle of separation of arsenic and antimony from copper is either distillation or gravimetric separation.

Distillation.—Two of the largest laboratories in the United States use some form of this method.

¹ J. Am. Chem. Soc., 26, 1647 (1904); also Eng. and Min. J., 75, 295.

² Eng. and Min. J., 89, 89 (1910).

If it is desired to estimate the antimony, as well, by evolution, a mixture made something like the following is used as a distilling solution for decomposition of the sulphides of the arsenic group, which are washed into the still with a little strong hydrochloric acid, completing the extraction from the paper with a few cc. of sodium sulphide solution, or the sulphides can be filtered on a felt which is transferred directly.

A.—Dissolve 150 grams of c. p. zinc in 140 cc. of hydrochloric acid (sp. gr. 1.2) and 440 cc. of distilled water, evaporate until the bulk is reduced to about 370 cc. Mix this solution with the solution of 100 grams of c. p. cupric chloride, dissolved in 330 cc. of concentrated hydrochloric acid. The total volume of mixed solution = 700 cc.

For slags, etc., take 30 cc., for refined copper 75 cc., of the solution, distil down in the flask which is connected with a short vertical glass condenser, until a thermometer, in the neck of the flask, shows 120° C., then add 35 to 40 cc. additional acid liquid and distil again. The condenser dips under water in a No. 3 or No. 4 beaker, and the distillate is finally removed and titrated with iodine as shown later under the "titration of arsenic."

A clean beaker of water is then placed below the condenser and the attempt is made, I understand, at two laboratories, to recover antimony by a further distillation at 122 to 160° C.

The antimony may be separated gravimetrically by separating its sulphide from the copper by extraction with dilute sodium sulphide solution (sp. gr. 1.08) and from the trace of tin, which is due to reagents and distilled water, by repeated precipitation and filtration in small volume (25 to 50 cc.) of concentrated oxalic acid.

B.—The iron precipitate, obtained as described under method C. is washed into the Allihn flask, by 100 cc. of strong hydrochloric acid, and then neatly reduced with about 5 cc. of 50 per cent. hypophosphorous acid, and distilled at a temperature below 120° C. The condenser dips under water in a No. 3 beaker, and the distillation is repeated with 50 cc. more of the acid. In the writer's opinion, a third distillation should then be made into a beaker of fresh water, which is separately titrated, and the process continued until the distillate shows no more traces of arsenic than one can always expect from the best acid.

Fifty cc. of concentrated zinc chloride solution are then added (W. H. Bassett's method) and the distillation continued at a temperature above 122° C. to evolve the antimony.

In the writer's experience, this distillation process is uncertain and requires repeated treatments to be sufficiently accurate for refined metal. The following gravimetric methods, accordingly, are to be preferred:

C.—Gravimetrically, by separation with large excess of iron salts and ammonia. Place the clean weighed copper drillings in a beaker, and dissolve on a steam plate in strong nitric acid (sp. gr. 1.42).

For refined copper, containing less than 0.03 per

cent. arsenic, we take 50 grams of copper, and treat with 210 cc. of acid, in a No. 7 beaker, but in the case of more impure material, it is sufficient to take 25 grams, or less, and treat in a No. 5 beaker (capacity 500 cc.) with 110 cc. of acid.

Dilute with water until the beaker is nearly half full, and add, to each assay, a solution of 2 grams of c. p. crystallized ferrous sulphate, which has been oxidized in a small beaker by heating with excess of nitric acid.

Heat nearly to boiling, and add strong ammonia until the iron is precipitated and the copper salts redissolved.

Fifty grams of metal will require about 300 cc. of ammonia. Heat to boiling, settle one-half hour on steam plate, and filter quickly through a 15 cm. washed filter, supported by a platinum cone with coarse perforations. It is necessary to keep the solutions warm to prevent crystallization, and the blue color is washed out of the filter with water made slightly alkaline ($1\text{NH}_4\text{OH}:10\text{H}_2\text{O}$).

If the bismuth is to be determined with antimony, add 2 grams of ammonium carbonate and 5 cc. of saturated sodium phosphate solution to the solution as soon as the iron is precipitated as hydrate.

When the sample contains less than 0.100 per cent. arsenic + antimony, the filtrate is passed through a second filter, to recover any traces of iron mechanically lost in the first washing.

If the copper is more impure than the above limit, make the blue filtrate acid with nitric acid, add 0.500 gram of the oxidized ferrous sulphate, and precipitate and filter again to clear the solution.

Redissolve the large precipitate in dilute sulphuric acid, treat the filter paper with a little ammonia, precipitate again, and pass through the same filter. If a second iron precipitation was made, dissolve this small amount of iron, add it to the blue filtrate from the last treatment of the major precipitate and add excess of ammonia and filter on a small filter.

Combine the two precipitates, dissolving them in hot, dilute sulphuric acid, containing .5 per cent. by volume of hydrochloric acid, and throw down the arsenic, etc., with the last traces of copper, by 15 minutes' cold treatment with a stream of hydrogen sulphide.

Allow to stand until granular, and well settled, then, before night, charge again with the gas and allow to settle over night.

In the morning, pass gas again until the solution smells strongly, and filter on a 7 cm. filter, then wash the beaker and tube by rubbing with bits of filter paper. Transfer paper and contents to a small, No. 6 beaker.

By the double gas treatment before filtering, the arsenic is generally brought down with the copper, instead of after it, but the filtrate should be charged with gas again and allowed to stand, until settled, and the operation repeated until precipitation is complete. We dissolve the sulphides of arsenic and antimony with traces of tin by hot digestion with sodium sulphide, using as little as possible, and washing, by stirring and pressure, with slightly alkaline hydrogen sulphide

water. Heat and filter again if any copper goes through, add 0.2 gram solid sodium hydrate, or potassium hydrate, and evaporate to dryness on the steam plate, then treat the residue with about 20 cc. of the strongest fuming nitric acid, and digest until the sulphur is dissolved.

The method of oxidation of sulphides with hot hydrochloric acid and potassium chlorate sometimes involves a loss of arsenic.

Remove the cover from the beaker, if the arsenic is to be subsequently weighed, and evaporate to dryness again.

If the arsenic is to be separated from other elements, the following method used in Montana is found to be superior to distillation.

Dissolve the dry residue in 25 to 50 cc. of hydrochloric acid (2 parts of acid (sp. gr. 1.2) and 1 of water), adding a small crystal of tartaric acid. Precipitate the arsenic from a cold solution with hydrogen sulphide, allow to settle for a short time, and filter on an asbestos felt, and wash with acid of the same strength.

As soon as the filtrate is washed out and sulphide wiped from the beaker with a little asbestos, the filtrate can be removed and the acid removed from the felt with some H_2S water.

Test the acid solution again and if no more arsenic appears throw down the antimony and traces of tin and copper with H_2S gas.

Selenium or tellurium, if present in sufficient quantity to interfere, may be removed by reducing the HCl solution with sodium sulphite or SO_2 gas before the H_2S treatment.

It has been observed that distilled water, unless condensed in iron or glass, as also the ammonia and HCl, generally shows a trace of tin, and a blank test of the acids reveals a trace of arsenic but, rarely, antimony. The felt, with the sulphides, is placed in a small beaker, the sulphur dissolved by digestion on the steam plate, with red fuming nitric acid, the solution diluted with one and one-half parts of water, the asbestos filtered out, and the solution evaporated to dryness on the steam plate, with 0.1 to 0.5 gram of sodium nitrate, according to the amount of arsenic present, if the latter is to be weighed as magnesium pyroarsenate.

Dissolve the residue in 5 cc. of cold water, with the addition of 10 drops of HCl, and 0.1 gram of tartaric acid.

Filter through a $2\frac{1}{2}$ -cm. filter into a 25-cc. beaker, unless the arsenic is known to be over 0.05 gram, and wash with as little water as possible from a fine jet. Make slightly alkaline with ammonia, when the liquid should be clear and not have a volume of more than 11 cc.

Add 3 cc. of magnesia mixture, make up to 20 cc. with strong ammonia and stir 5 minutes. If the arsenic is excessive, increase the precipitant and dilute with ammonia so that the total volume shall be 25 to 30 cc., of which one-third is free ammonia water.

Allow to stand over night in a cool place, filter on

a 2½ or 3 cm. filter, aiding the transfer of the arsenic by the filtrate.

Wash with a fine jet of ammonia (1 to 3 of water) until free from chlorine, dry in an oven, remove the salt to a glazed paper, and place the filter in a porcelain crucible.

Add a few drops of acid ammonium nitrate solution, (saturated), char carefully, and repeat treatment until the paper is consumed without a perceptible odor of arsenic.

Transfer the remainder of the precipitate and ignite at a full red heat over the Bunsen burner to a constant weight. The Mg mixture, Fresenius' formula, is as follows: 1 part of magnesium sulphate crystals, 4 parts of ammonium chloride, 8 parts of water, and 4 parts of concentrated ammonia (sp. gr. 0.90). The Mg should be free from lime and the mixture should not be used after it has attacked the bottle and dissolved glass from its interior.

COPPER FREE FROM ANTIMONY.

D.—Dr. Hampe, the German pioneer in accurate copper analysis, invented the method involving the reduction of the solution of copper by sulphurous acid gas with the removal of selenium and tellurium, and the subsequent precipitation of the copper as the white sulphocyanate. Dr. H. F. Keller has given a good account of this familiar but somewhat tedious method, and the reader is referred to his paper for details.¹

Lake Superior metal, not electrolyzed, rarely contains antimony, hence it is not necessary to make the separation in (2:1) HCl if water free from tin is used or the arsenic is to be titrated instead of weighed.

NEW VOLUMETRIC AND ELECTROLYTIC METHOD.

E.—This scheme of direct titration of an electrolyte is believed to be a new one, and will be found to permit much more rapid work with all classes of material, containing little antimony, and can also be used with any copper by preparing the solution for electrolysis,² separating the antimony and tin, if present, by methods previously published.

Such a method is adapted to routine control of impure material and was developed for the assay of a large tonnage of Lake copper, now produced, which runs high in arsenic, but has almost no antimony.

First. Modification for Copper with Less than 0.01 Per Cent. of Arsenic; without Antimony.—Dissolve the metal and separate the arsenic group as in method C, or perhaps D, but omit the final precipitation with hydrogen sulphide gas in (2:1) hydrochloric acid, as a trace of tin does not affect iodine in titration. In the rare case in which a trace of gold or platinum is present, the copper can be originally dissolved according to the method just devised by the writer, and which will be made the subject of a paper, at once, on a "New Method for the Determination of Gold in Copper Bullion."

Weigh 1 assay ton of very fine drillings (taken with a ¼" drill) into a No. 4 casserole, add 25 to the 30

grams of c. p. solid potassium bisulphate and 100 cc. of concentrated c. p. sulphuric acid, cover, and boil carefully on a gauze, or plate, for 10 minutes, when metal should be practically dissolved.

Decant acid, without diluting much if possible, and boil any little residue with a little more acid mix., then dilute, settle, and filter out gold and platinum. If selenium or tellurium is present, it can be reduced from the hydrochloric acid solution of the residue, obtained by evaporation of the first sodium sulphide solution of the arsenic group with fuming nitric acid. Treatment with sodium sulphite will effect reduction, or hydroxylamine as recommended by Dr. H. F. Keller.

The titration of an electrolyte gives a little too high results on arsenic, when the arsenic is less than 0.01 per cent. because of the presence of a minute trace of platinum which may be found in the electrolyte, and in much of the cathode copper, produced in the laboratory by the regular 5-gram battery assay of refined copper.

Whether it has been found necessary to purify the arsenic sulphide from traces of antimony, Pt and Se, or not, the residue from evaporation of the sulphide with fuming nitric acid and excess of soda is taken up with sulphuric acid, or better, 25 cc. of strong sulphuric acid are added to the nitric acid solution of the arsenic as soon as the sulphur has disappeared. Instead of a little sodium nitrate which was recommended in the gravimetric method to hold the arsenic, we add 3 grams of solid potassium bisulphate, free from chlorides. This is adapted from Low's method for ores.¹ Heat rapidly on a hot plate until the sulphuric acid fumes for 5 minutes.

Cool, wash into a 300 cc., long-necked Kjeldahl flask of Jena glass, place in an inclined position on a lamp stand over a small flame, boil off the water, fume 5 minutes again, and when the time is nearly up, flash the neck of the flask with a lamp flame, long enough to drive out any condensed liquid from the neck.

This double fuming process, and removal thereby of the last trace of nitric acid, is the *secret of success* with the process, as in the iodide method for titration of copper.

After the flask has cooled a little, add from a paper 0.5 gram of solid tartaric acid and, giving the flask a whirling motion occasionally, digest until the solution is colorless.

Allow to cool, wash into a No. 3 beaker, in which a little water has been placed, and fill the beaker about half full.

One advantage of this scheme is that a dozen digestions can be carried through as easily as one. Drop a small piece of litmus paper into the beaker, add ammonia until the liquid is just alkaline and bring back to the acid condition with dilute sulphuric acid, adding only one drop in excess.

Place the beakers in a large pan of water to cool, when they will be ready for titration with iodine.

This titration will be taken up after the description of the second electrolytic process.

¹ J. Am. Chem. Soc., **16**, 784 (1894).

² *Ibid.*, **26**, 1120 (1904).

¹ "Technical Methods of Ore Analysis." q. v.

E—2d part. Electrolysis followed by direct reduction and titration. This is the quickest of all methods for control work, and is accurate for any copper containing more than 0.01 per cent. of arsenic, and no more than a trace of antimony, but the latter if present would have to be removed unless it was permissible to neglect its influence.

If the metal contains less than 0.1 per cent. of arsenic, we take two portions of 10 grams of drillings and place them in the beakers used for the usual battery assay of copper, as described in the first paper.

Dissolve in a slight excess of strong nitric acid (sp. gr. 1.42), add 17 cc. of strong sulphuric acid and evaporate to dryness.

A whole set may, of course, be started at once, and when dry, and the residue smells sweet, add 12 cc. of nitric acid, and water sufficient to cover the electrode, which has the usual dimensions for copper assaying, about 100 sq. cm., counting both sides of the plate.

Pass a current of N. density = 1 ampere until colorless, then reduce to one-half an ampere; in short, perform the regular electrolytic assay for refined copper, just as described in the writer's first paper.

The small portion of liquid, removed for test, is washed into a little beaker, treated with a small crystal of potassium bisulphate, or sodium nitrate, and a few drops of sulphuric acid and evaporated until the sulphur is gone when it is transferred to the main solution now free from copper, which is treated with 3 grams of the solid potassium bisulphate, and evaporated until the nitric acid is all driven off and the sulphuric acid has fumed strongly for 5 minutes.

The solution is then washed into a Kjeldahl flask and digested as already described. In very accurate analyses, the first copper cathode is redissolved in 40 cc. of "Stock Solution" as described in the paper on the electrolytic assay, and the copper again deposited and the second electrolyte boiled down with the first.

The "Stock Solution" mixture of dilute acids is not employed for the original solution of the drillings because it is necessary to oxidize all the arsenic to the condition of arsenic acid, or there appears to be some loss—due to the electric current.

If the metal has more than 0.1 per cent. of arsenic, two 5-gram assays are taken, using 15 cc. of sulphuric acid and a final addition of 10 cc. of nitric acid for each. If 0.2 per cent. of arsenic is known to be present, each of the assays is boiled down, reduced and titrated separately, or if the arsenic is less, they may be combined as one and boiled together.

If the arsenic is between 0.01 per cent. and 0.05 per cent., two 10-gram assays are combined. The remarks on replating apply here.

A blank should be made with each new lot of acids, and digested. If selenium or tellurium is present, we dilute the dry residue of copper sulphate with water and reduce this element with excess of sodium sulphite free from chlorine, or with a rapid current of sulphurous acid gas at a temperature of 40° C., filter and allow to settle, before adding the nitric acid.

Notes on the titration of arsenious acid by iodine will follow.

If very rapid work is necessary, the solution can be electrolyzed for removal of copper in the rotary device, if water-cooled, but more traces of platinum are introduced into the electrolyte, and affect the iodine in titration.

In presence of antimony, the electrolyte can be boiled down until the nitric acid is off, then diluted with one and one-half volumes of water, and strong hydrochloric acid added in amount equal to the total and the arsenic separated by treatment of the cold liquid with excess of hydrogen sulphide.

Even with this modification, this method is more rapid than the gravimetric or distillation, particularly as a number may be done at once, in conjunction with regular copper determinations.

A few words may be of interest in description of a large rotary device which is of great assistance in removing the copper from solutions of either 25 or 50 grams of metal, in order that the electrolyte may be evaporated down to small bulk for the estimation of iron, zinc, nickel, cobalt, lead, etc., and, with an extra precaution to separate a trace of platinum, may be used to determine arsenic.

Dimensions: Size of beaker, No. 4 and 5 low form, capacities 500 to 750 cc., permits the passage of 6–8 amperes, or more, of current through the coil and solution by water-cooling the space between beaker and cylinder.

The anode is a straight doubled wire, and the cathode is a large, closed cylinder of foil, 7.5 cm. in diameter, 11 cm. high, and perforated with holes 3 mm. in diameter and spaced 1 cm. apart.

In the iron determination, 25 grams of drillings are dissolved in 25 cc. nitric acid, 40 cc. sulphuric acid and 100 cc. of water; 50 grams would require 55 cc. of nitric acid, 80 cc. of sulphuric and 250 cc. of water. 20 grams of copper for sulphur determination would be dissolved in 120 cc. of pure nitric acid and free acid removed before diluting with water. For arsenic test, 25 or 50 grams of metal are dissolved in nitric acid, either 40 cc. or 80 cc. of sulphuric acid and the nitric acid evaporated, until the residue smells sweet, after which 25 or 50 cc. of nitric acid are added and residue dissolved, and electrolyte dissolved and electrolyzed it has a chance to crystallize.

The use of the large rotary device is a success for the rapid separation of copper from most of the elements mentioned, but does not give as good results for arsenic as the electrolysis of 5 or 10 grams by the slow method. It requires that a precipitation of the arsenic be made in (2:1) HCl to remove not only antimony but also a trace of platinum which is dissolved continuously from the anode by the nitrous acid and heavy current.

Notes on the Accurate Titration of Arsenious Acid by Iodine.—We have made many experiments to ascertain the proper conditions for the accurate titration of arsenious acid in either very small, or large amount, and to eliminate slight errors which some

chemical authorities have declared to be inherent in the titration.

In the first place we have found that sulphuric acid is a better medium than hydrochloric acid for final solution and neutralization.

The blank tests for arsenic in the former acid or for the nitric acid used in the process are very small, but hydrochloric acid contains a variable trace of arsenic or element which distils and affects iodine.

The following are tests on two lots of c. p. HCl, from two makers.

No.	Cc. acid taken.	Cc. of iodine.	Blank for end-point.	Cc. of iodine.	Arsenic found Grams.
1.....	100	0.22	0.08	0.14	0.00015
2.....	100	0.32	0.08	0.24	0.00027

The HCl was neutralized with ammonia, using a piece of litmus paper as indicator, cooled, made acid with one drop excess and treated with 12 grams of sodium bicarbonate; total volume, 300 cc.

The soda should be free from iron.

We also find that the titration of traces of arsenic is rendered exact if three drops of a 10 per cent. solution of potassium iodide are added. This supplies the conditions for a clear end-point with 2 cc. of a starch solution made up according to directions recently published.¹ That authority directs that the starch shall be soaked 24 hours in very dilute HCl, then washed, dried, and heated 3 hours in a hot oven at 100° C. The end-point thus obtained is a remarkably delicate blue, free from the muddy reddish tint given by ordinary starch indicator, and the blank for the amount to produce an end-point is only 0.04 cc. of iodine, of which 1 cc. = 0.001 gram of arsenic.

Most of the printed methods direct that 2 to 4 grams of sodium bicarbonate should be added to the slightly acidified solution before titration. In the titration of large quantities, or any unknown assay, we find it is an advantage to add a very much larger excess of pure soda, free from iron, as it insures a sufficient quantity of the ions present, which recent investigators have said to be necessary for the uniform action of the iodine, and production of the iodide of starch. The use of the precautions mentioned, with cooling of the solution before the final addition of the bicarbonate of sodium, enables an operator to titrate a milligram of arsenic or 100 mg. as closely as one can precipitate it by magnesia and weigh it, and with more certainty for small amounts.

The iodine solution is made by dissolving 3.5 grams of pure resublimed iodine and 7 grams potassium iodide in water, diluting to one liter, and allowing to stand in a brown bottle for at least 24 hours before use.

A 10 per cent. solution of potassium iodide is also made and 3 or 4 drops are added to every titration, after the bicarbonate of soda.

Standardize with pure arsenious acid, of which 0.06-gram portions are dissolved cold in a little water containing 1 gram, or less, of potassium hydrate, washed into a No. 3 beaker, diluted to nearly 300 cc.,

made slightly acid with sulphuric acid, using litmus paper as an indicator.

Make slightly alkaline with ammonia, then faintly acid with one drop in excess of the acid, add the carbonate, and titrate rapidly until the end-point is nearly reached, employing 3 cc. of starch solution as the indicator and 3 drops of the 10 per cent. solution of KI.

The beaker is allowed to stand on a white surface, and a fainter end-point is noted and taken with less than 5 mg. arsenic, than when the quantity is large.

A table shows the agreement in the titration of varying amounts of arsenic with ordinary untreated starch indicator, which causes a higher blank test as shown. Results with the new starch are better, so much so that we now prefer to titrate arsenic in accurate analysis, rather than to weigh it.

As. taken.	Iodine, total cc.	Blank test.	Net cc. of iodine.	Arsenic found, gram.
0.0010	0.99	0.09	0.90	0.0010
0.0020	2.02	0.09	1.93	0.00214
0.00206	1.86	0.09	1.77	0.00196
0.0024	2.27	0.09	2.16	0.0024
0.0020	1.91	0.09	1.82	0.00202
0.00998	9.12	0.09	9.03	0.01002

A thermometer is attached to the burette, when standardizing and during the regular work, and a correction is made to the burette readings for changes in the volume of the solution from that prevailing at the time of the standardization.

CALUMET & HECLA SMELTING WORKS,
HUBBELL, MICHIGAN.

THE ESTIMATION OF VERY SMALL AMOUNTS OF CALCIUM BY MEANS OF POTASSIUM PERMANGANATE.

By L. T. BOWSER.

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The well-marked difficulties attending the use of both the potassium oleate and the turbidity method for the determination of small amounts of calcium suggested the advisability of working out some procedure as simple as either of these but more accurate, as well as less subject to defects. At the time this matter claimed attention the writer had just completed a method for the estimation of potassium in very small amounts as the cobalti-nitrite, titrating the precipitate with very dilute potassium permanganate, and the idea occurred that a similar procedure might serve for the estimation of calcium. Preliminary trials showed that it was entirely feasible to do this, and a careful investigation was made to determine the best conditions for accurate work. The results obtained and conclusions drawn may be of interest to others, hence will be briefly presented.

The method is essentially an extension of the well-known permanganate titration, so carried out as to be applicable in cases where calcium is reckoned only in parts per million. To the solution to be tested, of a volume of from 5 to 10 cc., a few drops of ammonium hydroxide are added, then about 0.4 gram of powdered ammonium chloride. It is then heated to boiling and 0.2 gram powdered ammonium oxalate added, the boiling being continued for a moment in order to make the precipitate as granular as possible.

¹ Chem. Abs., 4, 2617 (1910).

This boiling is best accomplished by setting the beaker, not over 50 cc. in capacity, on a wire gauze with Bunsen burner below. For the comfort of the analyst's hands it is well to use a circle of asbestos paper to cover the entire gauze save for a circle in the center just large enough to admit the bottom of the beaker. After the completion of this boiling the solution in the beaker is diluted with approximately its own volume of 3 per cent. ammonia to prevent crystallization of ammonium oxalate, then allowed to stand for some time, preferably two or three hours if the best results are sought.

Filtration is carried out under suction, using a filter of the Shimer form with an asbestos pad about one-fourth of an inch in thickness. For such small amounts of precipitate as are involved a tube much smaller than that used in ordinary work is advisable. The one in use here is of one-half inch internal diameter and two inches length, fitted with a small perforated aluminium plate. After the precipitate has been collected on the asbestos pad it is thoroughly washed with 3 per cent. ammonia to free it from excess of ammonium oxalate. The wash liquid should preferably be hot, although practically as good results may be attained if it is cold. The pad is pushed out and placed in the precipitating beaker, then water enough added to thoroughly moisten the asbestos and give a few cc. in excess.

The precipitate is decomposed by 1 cc. of 1/1 sulphuric acid and titrated with $N/200$ KMnO_4 , the excess of KMnO_4 being titrated back by means of $N/200$ oxalic acid. All titrations are carried out with the titrated solution kept at nearly the boiling point. With a little practice the end-point of this reaction may be noted easily and with precision. From the results of the titration a blank, to be determined by a separate titration, must be deducted as an allowance for permanganate consumed by the asbestos, water and sulphuric acid used. The first blank titration of a pad of asbestos oxidizes out practically all the impurities, and a second one should be made for the real blank to be deducted. Practically all of the permanganate consumed is due to the 1 cc. of sulphuric acid, as ascertained by a number of trials, hence there is necessity for care that exactly the same amount be used every time. Almost every blank made by the writer has been 0.23 cc., although this figure would no doubt vary with the conditions. The same asbestos is used over and over again so long as it will make a good pad, and one blank serves for all. As many as 12 determinations have been made, using one portion of asbestos.

For some purposes sufficient accuracy may be attained by using for the titration an ordinary 50 cc. burette graduated to tenths of a cc., but for the most accurate work a small one graduated in fiftieths or hundredths is to be preferred, and this may, if desired, be read to two hundredths of a cc. There is in use here a 2 cc. size graduated in fiftieths for permanganate, and a 1 cc. graduated in hundredths for oxalic acid. Both are fitted with tips drawn out so fine that the drops are very small, a

size such that ten drops of solution which equals 0.15 cc. is very satisfactory. A short rubber tube between the burette and small tip, with a glass bead in the tube to take the place of the more usual stopcock, gives a very delicate and satisfactory control of the rate of flow. The burettes are filled by inserting the tip in the desired solution and drawing it up by suction, taking care to avoid contamination in any way. When these small burettes are used in titrating it is well to add the greater part of the permanganate by means of a 5- or 10-cc. pipette, then to complete the titration with the burette.

Permanganate in such a dilute state does not oxidize as much as it should by theory, and it is necessary to standardize it against a calcium solution of known strength, under conditions similar as regards concentration and manipulation to those met in actual practice. Thus a $N/200$ solution such as used here should by theory oxidize 0.1002 mg. Ca per cc., whereas it is actually equal to only about 0.0793 mg. No satisfactory explanation of this behavior can be made at this time, but the matter is being made the subject of a study from which interesting results seem probable. That the best possible results may be secured it is important that an amount of solution be taken, such that not less than 4 cc. of $N/200$ permanganate shall be required to oxidize the calcium present, preferably a somewhat larger volume, and the same precaution must be observed when standardizing the permanganate. In case smaller amounts are used than those specified, there seems to be a tendency toward high results. It will be readily seen that this is a matter involving the total amount of calcium present rather than its initial concentration, and very good results may be obtained on exceedingly dilute solutions by taking a large volume and evaporating to the desired concentration. It is necessary to work with a final volume of 5-10 cc. of solution in order to overcome, to as great an extent as possible, the solvent effect of the water present.

By the use of this method extremely accurate and concordant results may be obtained in nearly every case, provided due care is exercised. The following results, taken at random from a large number secured in trying out the method, are typical of what may be expected. Table I gives a series on which was based the standardization of the permanganate solution.

TABLE I.

No.	Cc sol. used	Cc KMnO_4 consumed	Mgm Ca used	Mgm Ca found	Parts per million used	Parts per million found
1.	10	4.300	0.3429	0.3410	34.29	34.10
2.	10	4.335	0.3429	0.3438	34.29	34.38
3.	10	4.315	0.3429	0.3422	34.29	34.22
4.	10	4.340	0.3429	0.3442	34.29	34.42
5.	10	4.345	0.3429	0.3446	34.29	34.46
6.	10	4.310	0.3429	0.3418	34.29	34.18
Aver.		4.324				

From the average amount of KMnO_4 used, 4.324 cc., we find that 1 cc. oxidizes 0.0793 mg. Ca., and from this the recorded amounts are calculated. It will be noted that the agreement here is very close for a method involving such minute amounts. In

Table II is shown the result of a series where the initial concentration was less and the total amount of lime greater.

TABLE II.

No.	Cc. sol. used.	Cc. KMnO ₄ consumed.	Mgm. Ca used.	Mgm. Ca found.	Parts per million used.	Parts per million found.
1.....	50	5.75	0.4285	0.4560	8.57	9.12
2.....	50	5.53	0.4285	0.4385	8.57	8.77
3.....	50	5.82	0.4285	0.4615	8.57	9.23
4.....	50	5.81	0.4285	0.4610	8.57	9.22
5.....	50	5.71	0.4285	0.4530	8.57	9.06
6.....	50	5.74	0.4285	0.4550	8.57	9.10
7.....	50	5.59	0.4285	0.4430	8.57	8.86
8.....	50	5.445	0.4285	0.4320	8.57	8.64
9.....	50	5.425	0.4285	0.4300	8.57	8.60
10.....	50	5.45	0.4285	0.4320	8.57	8.64
Aver.....						8.924

The agreement is not so close here, although toward the last of the set, as experience was gained, there was a considerable improvement. However, as a whole this series is quite satisfactory. What happens when too small a total amount of calcium is taken may be seen in Table III, the first five portions containing half the amount of the last six, and falling below the limit of 4 cc. of permanganate needed, equivalent to about 0.3 mg.

TABLE III.

No.	Cc. sol. used.	Cc. KMnO ₄ consumed.	Mgm. Ca used.	Mgm. Ca found.	Parts per million used.	Parts per million found.
1.....	50	3.34	0.2142	0.2650	4.29	5.30
2.....	50	3.28	0.2142	0.2600	4.29	5.20
3.....	50	3.40	0.2142	0.2695	4.29	5.39
4.....	50	3.31	0.2142	0.2625	4.29	5.25
5.....	50	3.27	0.2142	0.2595	4.29	5.19
Aver.....						5.27
6.....	100	5.31	0.4285	0.4210	4.29	4.21
7.....	100	5.49	0.4285	0.4360	4.29	4.36
8.....	100	5.46	0.4285	0.4330	4.29	4.33
9.....	100	5.44	0.4285	0.4320	4.29	4.32
10.....	100	5.45	0.4285	0.4330	4.29	4.33
11.....	100	5.44	0.4285	0.4320	4.29	4.32
Aver.....						4.32

This series is sufficient to satisfactorily illustrate the point that not less than 0.3 mg. of Ca should be present. This is the minimum limit, while there is apparently no maximum one. The last six results must be conceded to be exceedingly satisfactory, and constitute, along with those previously given, a very fair test of the capabilities of the method. It possesses a number of decided advantages over the other two, such as accuracy, speed, easy manipulation, and the absence of any necessity for preliminary decolorizing of a solution to be operated upon. The procedure outlined is in a measure adapted from the turbidity method used by the Bureau of Soils,¹ and prevents the danger of interference of magnesium. Uniformly good results have been secured by the method, and it is believed that its evident merits will commend it to those having occasion to estimate unusually small quantities of calcium for any purpose.

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LINSEED OIL.

By A. H. SABIN.

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It was observed some ten or twelve years ago by Weger and Lippert that a considerable proportion of their tests of drying linseed oil showed an increase of weight to a maximum and then a small decrease; but, with the exception of L. E. Andés, no notice seems to have been taken of this by recent writers, and it was in fact unknown to the present writer until this investigation had long been under way. It is generally assumed that this oil, when exposed to the air, absorbs oxygen, and that this is substantially all the action which takes place, although Toch has called attention to the fact that a small amount of CO₂ is evolved. Brooks has recently noted the presence of traces of formaldehyde and appreciable amounts of formic acid as oxidation products from this oil; although never published, these facts were known to the writer and to at least one other technical chemist many years ago.

Oil has long been oxidized by blowing air through it, usually with heat; if this operation is carried far enough, an insoluble product is formed, but this is different from the film of dried oil obtained when oil is dried in a thin film on glass or other support, being less perfectly oxidized. As the chief use of oil is in paint, it is best to conduct these experiments with films.

Glass plates, 4 x 5 or 5 x 7 inches, were used, as these can be weighed on a sufficiently delicate balance; these were coated with oil, both raw and boiled, and paints, the latter prepared by first ascertaining how many pounds of each pigment will make up, in paint, the volume of one gallon; for example, it is found that 55 lbs. of dry white lead, added to any quantity of oil or turpentine, increases the volume one gallon, whence it is inferred that 55 lbs. of white lead contain enough solid matter to measure 231 cu. in. Having determined these figures, paints were prepared by adding one-fourth of a gallon of pigment to three-fourths of a gallon of oil, or in that proportion, but in constructing the curves of drying, only the oil is taken into account, and the curves show the percentage gain or loss of the oil, as if no pigment were present; that is, the pigment is assumed to be inactive in all cases. These experiments were started about eight months ago, and in most cases four or six plates were coated with each preparation; very little variation was found between duplicates.

The boiled oil was ordinary raw oil cooked in a kettle with PbO and MnO₂, and contained the equivalent of 0.19 per cent. PbO and 0.023 per cent. MnO. The paints were made with raw oil, without driers.

It will be observed that raw oil rapidly increases in weight, gaining 16 to 18 per cent. in less than a week; the greatest part of this gain takes place before the oil begins to set or harden appreciably; then it loses weight rapidly but not as rapidly as it had gained, and in ten days or two weeks has lost about one-eighth its increment of added weight; then it loses more and more slowly, until in four months it has

lost three-fourths of the original increase, and in eight months about nine-tenths, and the curve is still approaching the base-line.

Boiled oil, singularly enough, gains much less than

The raw oil paints follow, as might be expected, the raw oil curve, but have some remarkable eccentricities, which future investigation will probably show to have significance.

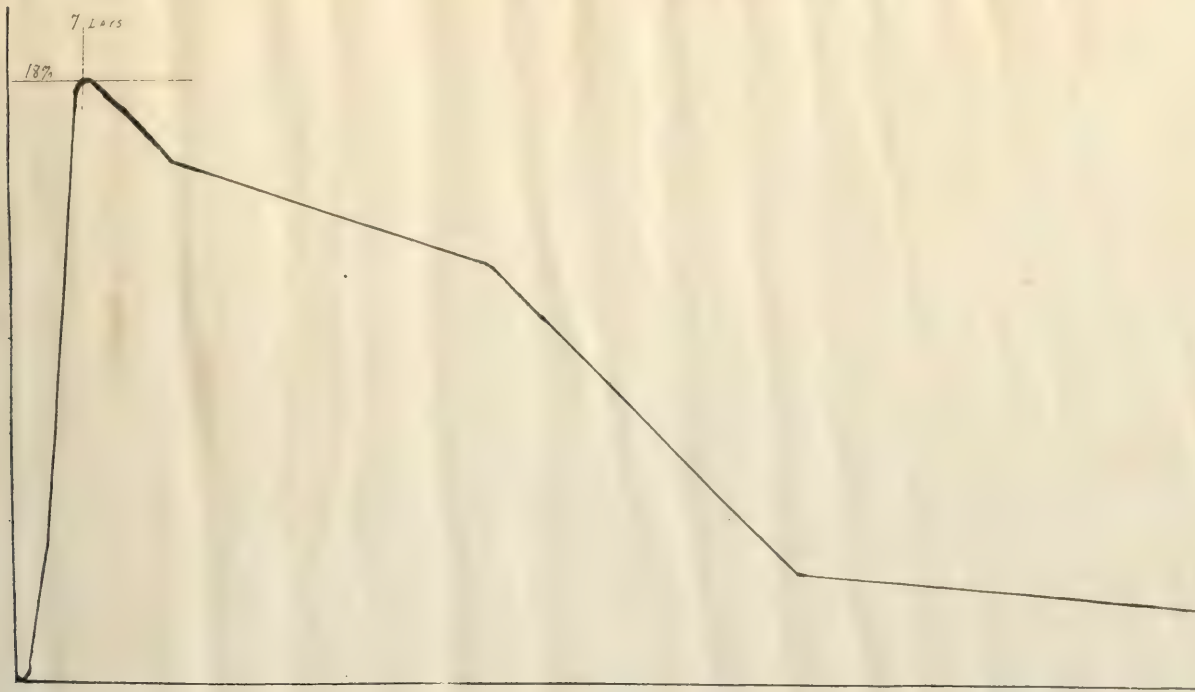


Fig. 1.—Linseed oil.

raw, reaches its maximum about the same time, then loses, showing a curve similar but less accentuated.

During the entire period, decomposition products are given off, most noticeably during the period of

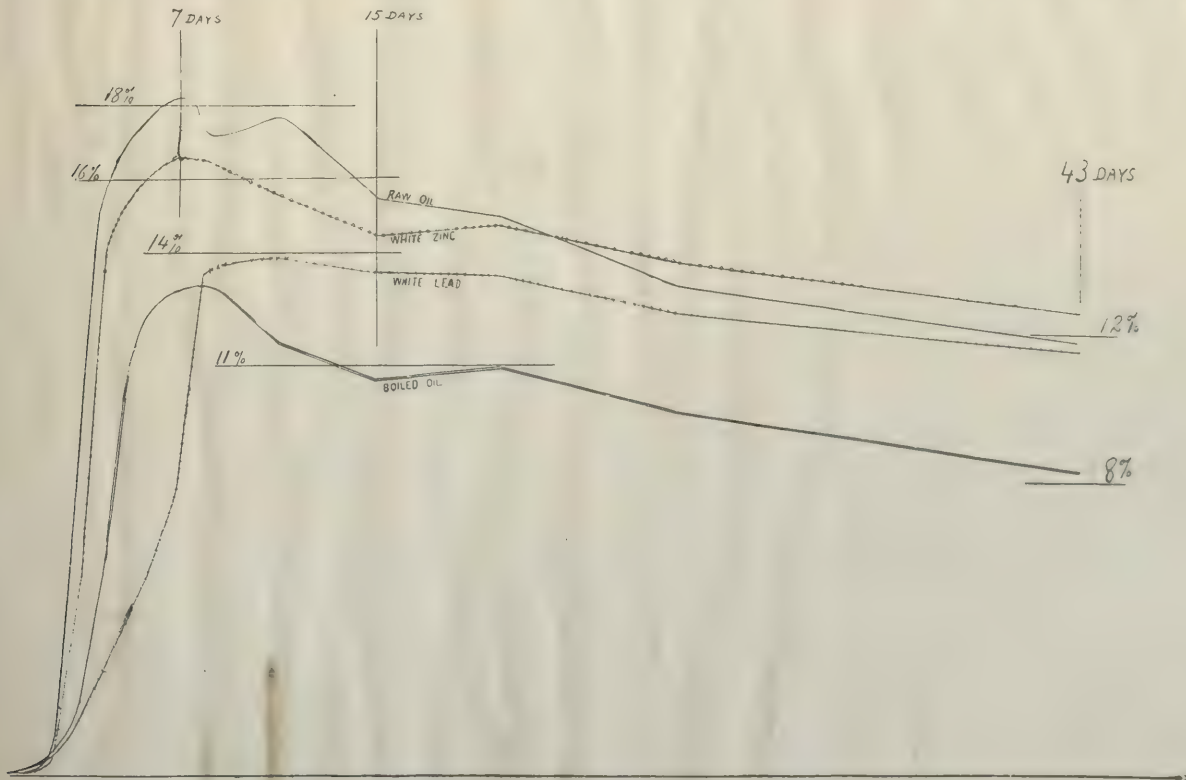


Fig. 2.

increase of weight, and the location of any point in the curve is possibly a result of partially balancing gains and losses. These are probably affected differently by atmospheric conditions, which accounts for the minor irregularities of the curves. The chart showing a single curve for raw oil is averaged from all the experiments with raw oil without pigments, and should be continued in the manner described.

It is also noteworthy that raw oil films eight months old show a specific gravity of 1.098 or about 18 per cent. more than the gravity of fresh oil. The gain in weight at this period is not more than 2 per cent., and this increase in gravity, which may be variously inter-

Storch reaction for colophony, the general consensus of opinion being that their indications are unreliable or of so little sensitiveness as to be practically valueless to the analyst for most purposes of identification; in many cases the author is in accord with this belief.

Nearly two years ago, however, there appeared an article by P. Foerster,¹ who pointed out the application of a color reaction, which had been devised some years previously by Halphen for the detection of rosin oil in mineral oils, to the detection of colophony in admixture with some other resins, which does not appear to have had the recognition from chemists who might be interested in it that it properly deserves.

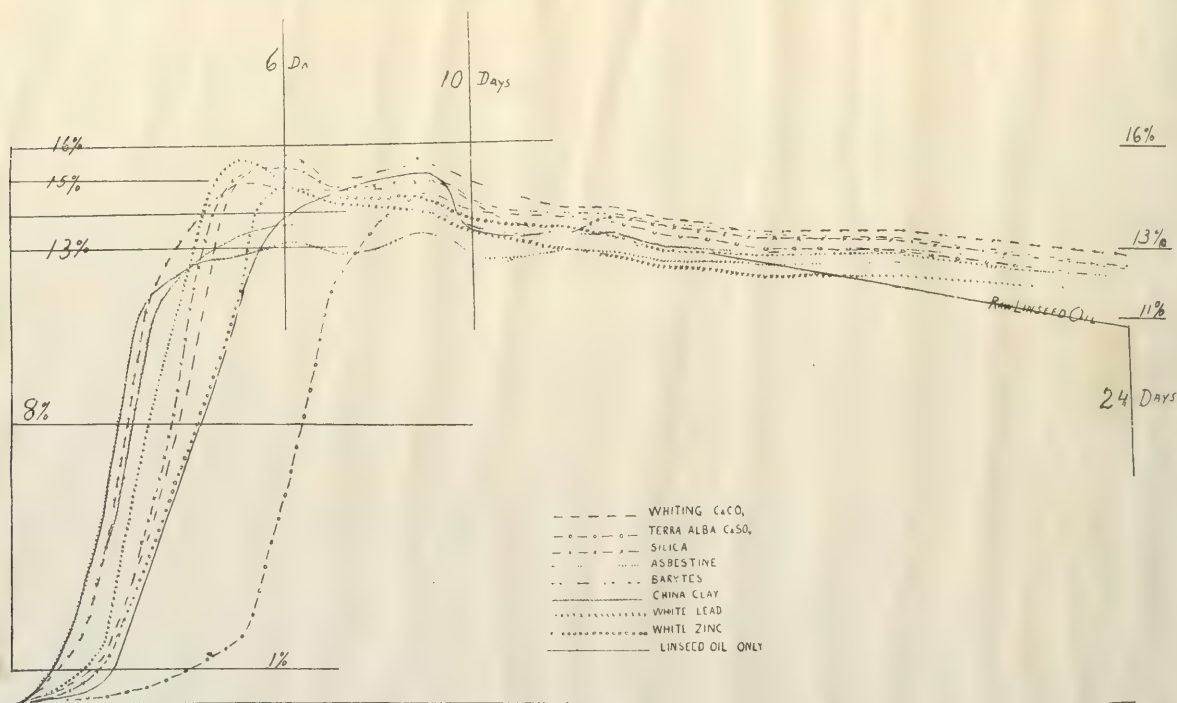


Fig. 3.

preted, at all events means a considerable shrinkage of volume, and is an important fact as to the way the lapse of time affects the character of the film.

The effect of pigments on these oil-carrying curves may perhaps be due, not to promoting oxidation, but to hindering peroxidation processes which involve loss of weight.

Acknowledgment of aid and cooperation is due to the staff of the Laboratory of the National Lead Co., and especially to G. W. Thompson, chief chemist.

NEW COLOR REACTIONS FOR SOME OF THE RESINS WITH HALPHEN'S REAGENT FOR COLOPHONY.

By EDWIN F. HICKS.

Received December 31, 1910.

Many color reactions for the identification or detection of various resins, either in their natural state or in admixture, have been proposed from time to time by a number of chemists, and some tables of these color reactions have been compiled and published, but none of them have met with general approval or extensive application, other than the Liebermann-

The test is simple of execution, and is an extremely sensitive and reliable color reaction for colophony, a minute quantity giving the characteristic color changes distinctly in a few seconds, and the reaction has the advantage of not being transient as is the case with the well-known Liebermann-Storch test.

The Halphen reagent consists of two solutions: (A) 1 part by volume of phenol dissolved in 2 parts of carbon tetrachloride and (B) 1 part by volume of bromine in 4 parts of carbon tetrachloride.

The procedure which I have found most convenient for conducting the test is as follows: A small quantity of the powdered resin, or the residue resulting from the evaporation of the ethereal extract of a larger quantity of the substance to be investigated, is dissolved in from 1-2 cc. of solution A. This solution is poured into one of the cavities of an ordinary porcelain color-reaction plate until it just fills the depression; a portion of the solution will soon be seen to spread out on the flat part of the plate a short distance beyond the rim of the cavity, unless too

¹ Ann. Chim. Anal., 14, 14 (1909).

much of the carbon tetrachloride has been lost through evaporation during the process of solution, when a drop or two more should be added to produce the spreading effect above referred to. Then immediately in an adjacent cavity of the plate a cc. or so of solution B is placed and the bromine vapors evolved are allowed to impinge upon the surface of the solution in the other cavity. Sometimes it is necessary to blow a gentle current of air in the proper direction to accomplish this satisfactorily, or both cavities may be covered by a watch crystal of suitable size.

The color reactions begin almost immediately with the contact of the bromine vapors and are best observed upon the flat portion of the test-plate. In most cases they last long enough for satisfactory observation; the changes in colors are practically over, however, in a period varying from five to ten minutes.

The sensitiveness and reliability of this reaction for detecting minute amounts of rosin in admixture with various substances led me to apply the same reaction to some other of the more common resins used in commerce, especially the varnish gums, and I have stated below in tabular form the results of my observations, first giving that already observed by Foerster in the case of colophony.

Colophony.—First green, then rapidly blue and violet; latter lasts considerable time, then slowly changes to purple, and finally a deep indigo in all parts.

Dammar.—Brown to lilac-brown, forms rather slowly; gradually changes into a distinct reddish brown (maroon).

Elemi.—Indigo-blue, forms at once, quite permanent; gradually deepens in color, sometimes becoming purplish, but generally remaining a dark rich indigo.

Kauri.—Azure-blue, changing rapidly to purple through violet shades. Later, at point farthest from bromine vapors a dark olive-green forms.

Manila Gum (spirit-soluble).—A very faint brownish green forms slowly; changes gradually to violet and finally purple. At point farthest from bromine vapors a chocolate-brown usually is produced.

Mastic.—Reddish brown, becoming almost a carmine nearest bromine vapors. A coffee-brown tint is produced at the far side of the test.

Sandarac.—Lilac forms almost immediately and is quite permanent; gradually changes to a violet, becoming violet-brown farthest from bromine vapors.

Shellac, (when pure.)—Gives no colorations.

Zanzibar Copal.—A light brown forms slowly, later brownish violet and finally a chocolate-brown mixed with some violet.

Of course the intensity of the colors and tints is to a degree dependent upon the concentration of the resin in the solvent solution A, but a little experience in the application of the test with materials of known purity will soon give one the ability to interpret the indications without difficulty.

In conclusion, I should state that I have not tested thoroughly the reliability of the color-reactions where several of those giving characteristic colors have been in admixture, but in a few cases that were tried

the results have given valuable indications, except that the reaction with common rosin is so intense that if present in the mixture in any considerable amount it is apt to mask the other color indications.

Perhaps it would be well to state also that the presence of more than traces of water, alcohol or ether interfere with the sensitiveness of the color-reactions.

ERRORS IN DETERMINING THE SIZES OF GRAIN OF MINERALS AND THE USE OF SURFACE FACTORS.¹

By HARRISON E. ASHLEY AND WARREN E. EMLEY.

Received December 27, 1910.

In the clayworking industry, the size of the microscopic grains is of great importance in regard to plasticity, rate of vitrification, warping, cracking, appearance, etc. This led us to a study of methods of determining the size of grain and of expressing the results numerically.

Diameters.—The size of microscopic particles is usually expressed in diameters. When we looked at our irregular clay particles, the effort to make them appear circular and then to read the diameter by the eye-piece micrometer exceeded the power of our imagination.

Equivalent Rectangle.—We were able, however, to construct mentally an equivalent rectangle, and to read its length and breadth.

Mr. A. V. Bleininger had previously done this and represented the size of particle as the square root of an area: $\sqrt{\text{length} \times \text{breadth}}$. A.

Volume of Grain.—The question remained, however, whether or not the depth of the grain bears a constant ratio to this figure.

Round Grains.—The round grained mineral with which we are familiar is the Illinois glass sand from Wedron and Ottawa. We were quite surprised

Edge by Microscope	$\sqrt{\text{length} \times \text{breadth}}$	(A)
Vol. " "	$(\text{length} \times \text{breadth})^{\frac{3}{2}}$	(B)
Wedron Sand No 2 Fireclay		
Vol. by Microscope	21.38 cu. mm.	.6898 cc.
Vol. by Weight	11.84 " "	.2203 "

Fig. 1.

to find it showing parallel rounded edges like a loaf of yeast bread. 28 grains of this sand were measured and their individual volumes calculated on the assumption $\text{Volume} = (\text{length} \times \text{breadth})^{\frac{3}{2}}$. B.

The weight of the same 28 grains was divided by the specific gravity of quartz, also to obtain the volume. The results were:

Volume by microscope.....	21.38 cu. mm.
Volume by weight.....	11.84 cu. mm.

Evidently the depth averages a little less than half expression A for this sand.

¹ By permission of the Director of the Bureau of Standards.

Sharp Grains.—A No. 2 fire-clay from Nelsonville, O., leaves sharp irregular fragments on a 20-mesh sieve. 50 of these grains showed:

Volume by microscope.... 0.6898 cc.

Volume by weight..... 0.2203 cc.

Here the depth is approximately one-third of expression A.

Flat Grains.—Evidently flat-grained minerals, like kaolin and mica, would give ratios far greater than these two cases.

This leads us to be very skeptical of most calculations based on the diameter of mineral grains as measured by the microscope.

Correct Size Measurements.—Zsigmondy¹ computed the size of gold particles from the concentration of the solution, the specific gravity of gold, and the observed number of particles in a measured volume, obtaining results free from objection. He made no conjecture as to shape of particle, avoided the use of the word "diameters," and assumed a cubical-shaped particle for computation purposes. This seems the most feasible procedure.

Group Classification of Clays.—Seger,² the founder of the scientific study of clayworking problems, found it convenient to classify the grains of natural clays in groups between definite size limits as follows:

		Average diameter.	Purdy surface factor.
Coarse sand.....	Over 0.333 mm.
Fine sand.....	0.333-0.040 mm.	0.1865	5.36
Silt.....	0.040-0.025 mm.	0.0325	30.77
Rock dust.....	0.025-0.010 mm.	0.0175	57.14
Clay.....	0.100-0.000 mm.	0.0050	200.00

Arithmetical Mean.—Mellor³ says: "A trial obtained by subdividing a given fraction shows that the arithmetical mean of the extreme diameters, namely, $\frac{1}{2}(d_1 + d_2)$, may be less or greater than the true average diameter. The validity of the arithmetical mean has been called in question by A. Heath⁴ and by A. S. Cushman and P. Hubbard.⁵ The deviation is greatest when the adjacent fractions are very large in proportion to the fraction under investigation."

Other Means.—Among other possibilities mentioned by Mellor are the geometrical mean, $\sqrt{d_1 d_2}$; E. J. Laschinger's "average diameter, $\frac{d_1 - d_2}{\log_e d_1 - \log_e d_2}$," and Mellor's average diameter, $\sqrt[3]{\frac{(d_1 + d_2)(d_1^2 + d_2^2)}{4}}$.

Von Reytt,⁶ using round-hole sieves, found the diameter of the mean particle passed by one sieve and retained by the next to be 0.87 times the diameter of the mean sieve hole.

As Von Reytt's results were obtained on so much larger particles, it is questionable whether we are justified in including them in the table below.

¹ Zsigmondy-Alexander, "Colloids and the Ultramicroscope" (1909).

² "Collected Writings, American Ceramic Society translation," p. 43 (1902).

³ Pottery Gazette, 35, 789; Trans. Eng. Cer. Soc., 9, 94 (1910).

⁴ Trans. Eng. Cer. Soc., 3, 23 (1904).

⁵ J. Am. Chem. Soc., 29, 589 (1907).

⁶ Richards, Ore Dressing, 1, 305; Oest. Zeit., 36, 229, 246, 255, 268, 283 (1888).

All of these formulas are equally as true for cubes as for spheres, save those involving length and breadth.

Law of Variation in a Group.—To investigate the reliability of duplicate measurements, we plot a sort of probability or variation curve, in which the measure-

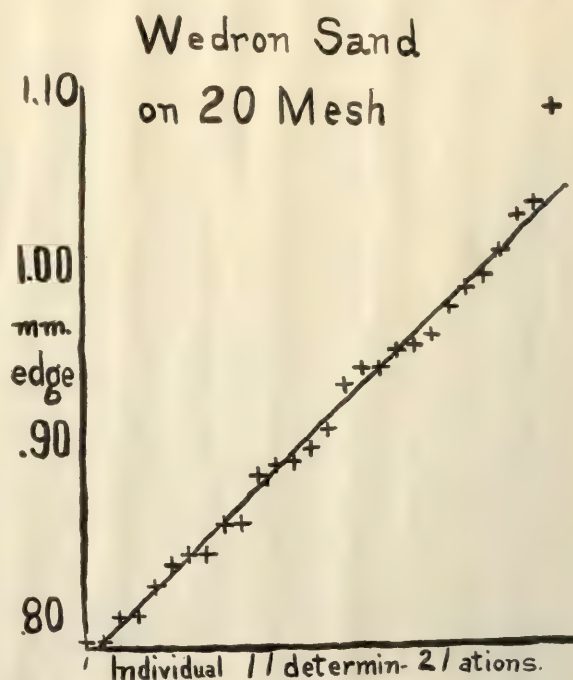


Fig. 2.

ments are plotted as ordinates, the lowest measurement having zero as abscissa, the next lowest 1, the

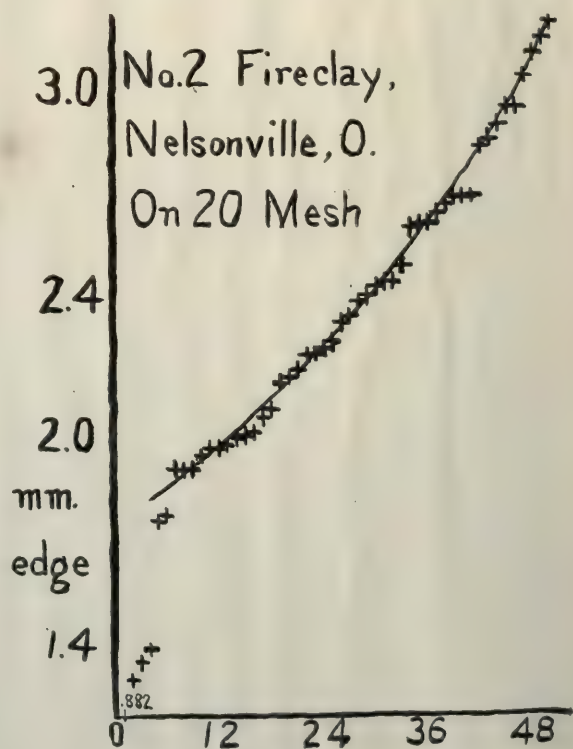


Fig. 3.

next 2, etc. If perfect duplicates were obtained, this would give a horizontal line.

Fig. 2 shows such measurements on Wedron, Ill., sand retained on a 20-mesh sieve. Practically a uniform

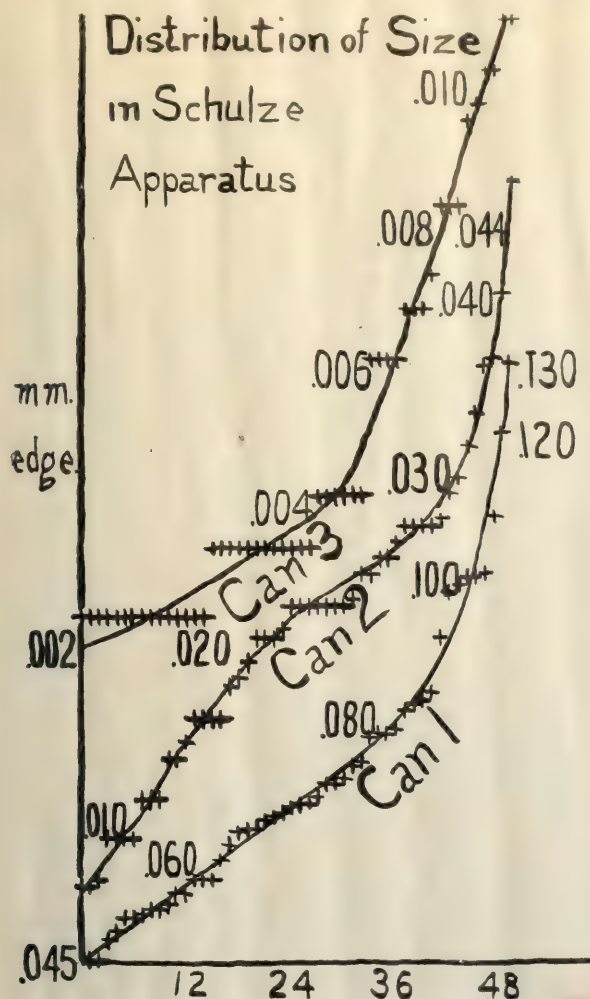


Fig. 4.

variation in size is shown. Fig. 3, No. 2 fire-clay retained on 20 mesh, deviates slightly from a straight line.

CALCULATED MEALS FOR TYPICAL CURVES.

	Can 1a.	Per cent. deviation.	Can 2a.	Per cent. deviation.	Wedron.	Per cent. deviation.
Max. edge, mm.....	0.13127	..	0.04682	..	1.032	...
Min. edge, mm.....	0.04498	..	0.00643	..	0.782	...
Edge of av. cube.....	0.07697	8	0.02462	16	0.905	0.6
Average edge.....	0.07143	..	0.02126	..	0.899	...
Arithmetical mean.....	0.08813	23	0.02663	25	0.907	0.8
Geometrical mean.....	0.07684	8	0.01735	-18	0.898	-1.0
Laschinger's mean.....	0.0807	13	0.0204	-4	0.900	0.1
Mellor's mean.....	0.0946	32	0.0310	42	0.912	1.4
Von Reytt's mean.....	0.0767	7	0.02314	9	0.789	-11

Fig. 4 shows 3 curves representing the silicious residues of a Tenn. Wad clay left in the 3 cans of a Schulze elutriating apparatus. Only can 2a shows the theoretical form of the probability or variation curve, while the can 1a and 3a curves are very concave.

Best Mean.—On the 3 forms of curve so found, the average edge (assuming cubical particles) is given in the above table, calculated by each of the methods, and also from direct measurement.

All apply well to the straight line (Wedron) save Von Reytt's.

Mellor's mean is least satisfactory for the elutriation residues, and the arithmetical mean nearly as bad. The geometrical and Laschinger means have deviations of different sign for the two kinds of elutriation residues. Von Reytt's simple empirical device seems (perhaps by chance) to give best results, and would have given better had a smaller constant than 0.87 been employed.

By examining grains by the methods given above it should be possible to accumulate data showing what form of mean is most reliable.

Surface Factors.—For many chemical and ceramic purposes, the activity of a material is considered proportional to its area.

For computing the area, surface factors are employed:

Rittinger's Law.—Rittinger¹ proved that the work of crushing is very nearly proportional to the reciprocals of the diameters crushed to, hence to the total surface of the resultant particles.

Stadler² falls into error in assuming that for crushing Kick's law holds that "the energy required for producing analogous changes of configuration of geometrically similar bodies of equal technological state varies as the volume or weights of these bodies."

Von Reytt's Factors.—Von Reytt³ confirmed Rittinger experimentally.

In computing the surface of a kilogram of material, for round-hole sieves, he used the factors 3.4 to $4.2 \times \frac{\pi(d_1 + d_2)^2}{4}$ and for square-hole sieves 4.0 to $4.2 \times \frac{\pi(d_1 + d_2)^2}{4}$.

This is the first use of a surface factor we have noted.

Moisture Surface Factor.—Von Reytt, following Rittinger's suggestion of measuring the adhering moisture, found that "while the adhering moisture is approximately proportional to the amount of surface on coarser

¹ Richards, *Ore Dressing*, 1, 304-10; Mellor, *Pottery Gazette*, 35, 687; *Trans. Eng. Cer. Soc.*, 9, 50 (1910).

² J. Chem. Met. Soc. S. Africa, 10, 382-91; *Chem. Abs.*, 4, 3059 (1910).

³ Richards, *Ore Dressing*, 1, 304-10; *Oest. Zeit.*, 36, 229, 246, 255, 268, 283 (1888).

⁴ When n is the number of particles measured.

particles, it does not hold on particles below 0.35 mm." A water surface factor was therefore impracticable.

Other Discoverers.—The idea of surface factors has also been worked out more or less independently by M. Whitney,¹ W. Jackson,² Arthur Yates,³ R. H. Richards,⁴ Algernon Del Mar,⁴ Wo. Ostwald,⁵ and doubtless numerous others.

Jackson's, Mellor's and Purdy's Factors.—Jackson's device was peculiarly lacking adaptation to different limiting sizes, and was simplified by R. C. Purdy. If dm is the mean diameter (mm.) of any group, W_m the weight of the group (expressed as a fraction of the total amount of material being tested), s the specific gravity, then $6W/dm$ is the surface of the same fraction of 1 mg. of the material.

The total surface⁷ of 1 mg. of the material is the sum of the surfaces of the several groups: $\frac{6}{s} \left(\frac{W_m}{d_m} + \frac{W_n}{d_n} + \frac{W_o}{d_o} + \dots \right)$ sq. mm. Owing to irregularities in the shapes of grains and to the errors discussed above in determining the mean diameter of a group the formula is only approximate, and Mellor employs it as an abstract number. As the materials used in clayworking (clays, kaolin, feldspar, quartz) have nearly the same specific gravity, Purdy threw away the factor $6/s$. The mining engineers, Yates, Richards, and Del Mar, follow Purdy's example exactly, though independently.

Whitney first calculated the approximate number of grains per gram by the formula $\frac{a}{A} \cdot \frac{6}{\pi d^3 s} = n$ and then the surface area by the formula $\pi d^2 n$. In these formulas

n = the number of grains in one of the mechanical analysis residues;

a = the weight of the group;

A = the total weight of the sample;

$a/A = W$ = the fractional portion of the whole in any one of the mechanical analysis groups;

d = the mean diameter of the group;

s = the specific gravity;

By substitution, the surface area = $\pi d^2 \cdot \frac{a}{A} \cdot \frac{6}{\pi d^3 s} =$

$$\frac{6}{s} \frac{W}{d}$$

Whitney's two formulas give identically the same result as the single formula now advocated by Mellor.

Whitney preceded all but Von Reytt, but used not a single factor but the product of two factors, giving the same result as Mellor's form.

Limiting Sizes for Groups.—In our present condition of inexact knowledge as to the laws governing the variation of size of particles, it is exceedingly important,

¹ U. S. Weather Bureau, *Bull.* 4, 40; Wiley, "Agricultural Analysis," I, 251-254 (1894).

² *Pottery Gazette*, 25, 1126 (1904); *Trans. Eng. Cer. Soc.*, 3, 16 (1904); "A Text-book of Ceramic Calculations," London, 22 (1904).

³ *J. Chem. Met. Soc. S. Africa*, 9, 187-91; *Chem. Abs.*, 3, 2672 (1909).

⁴ *Mining and Sci. Press*, 101, 614-15 (Nov. 5, 1910).

⁵ "Grundriss der Kolloidchemie," pp. 80-81, 84-87 (1910).

⁶ *Trans. Am. Cer. Soc.*, 7, 441 (1905).

⁷ J. W. Mellor, *Pottery Gazette*, 35, 788; *Trans. Eng. Cer. Soc.*, 9, 94 (1910).

for comparable results, that the same limiting size of group be used by all workers. Especially is this true of the smallest fraction, consisting of particles assumed to range in size down to zero. Mellor has indeed proposed and strongly insisted on certain definite limits, but only with the object of obtaining fractions that can be graphically represented on a triaxial diagram.

Effect of Varying Limits.—A partly assumed case will show the results of using the limits of Seger, Purdy, and Mellor in computing Purdy's surface factor.

Purdy¹ gives the following mechanical analysis of a clay, K_3 , using arithmetical means:

Purdy's group limits.	Mean diam. (dm).	$1/dm$.	Per cent.	Per cent./100 $\times 1/dm =$ Purdy's surface factors.
On 1 mm. sieve....	1.25	0.8	1.50	0.012
1-0.1 mm.....	0.55	1.82	2.41	0.044
0.1-0.01 mm.....	0.055	18.2	57.15	10.34
0.01-0.001 mm.....	0.0055	182.	25.14	45.78
0.001-0 mm.....	0.0005	2000.	13.96	279.4
			100.16	325.6
				Total sur- face factors.

If we take Seger's limits, and assume uniform variation in each of Purdy's groups, the following rearrangement may be obtained:

Seger's group limits.	Mean diam.	$1/dm$.	Per cent.	Per cent./100 $\times 1/dm =$ Purdy's surface factors.
Above 0.333 mm....	0.9165	1.091	3.29	0.036
0.333-0.04 mm.....	0.1865	5.37	38.70	2.075
0.04-0.025 mm.....	0.03125	32.08	9.54	3.06
0.025-0.010 mm.....	0.0175	57.02	9.54	5.44
0.010-0 mm.....	0.005	200.	39.10	78.2
			100.17	88.811
				Total sur- face factor.

Mellor's limits, on the same assumptions, give:

Mellor's group limits.	Mean diam. ²	$1/dm$.	Per cent.	Per cent./100 $\times 1/dm =$ Purdy's sur- face factors.
Above 0.107 mm....	0.8035	1.244	3.89	0.0484
0.107-0.063 mm.....	0.085	11.76	23.49	2.77
0.063-0.010 mm.....	0.0365	27.41	33.68	9.23
0.010-0 mm.....	0.005	200.	39.10	78.2
			100.16	90.25
				Total sur- face factor.

Predominating Effect of Smallest Groups.—When the mechanical separations end at 0.010 mm., as in Seger's and Mellor's work, the final fraction (0.010-0 mm.) will have equal and predominating weight (78.2) in both the total surface factors. Only 1.6 per cent. variation in total surface factor is caused in this case by changing from Seger's to Mellor's group limits. But if the group 0.010-0 mm. is subdivided at 0.001, as is done by Purdy and others, including our agricultural chemists, then the numerical value of the total surface factor is enormously increased.

Seger's Limits Preferable.—It is a difficult matter to say what limits should be chosen, but the senior writer having used Seger's limits for several hundred

¹ Illinois State Geological Survey, *Bull.* 9, 152 (1908).

² This is not Mellor's mean, but the arithmetical mean.

mechanical separations¹ has been deeply impressed by their practical utility.

Existence of Exceedingly Fine Mineral Crystals Doubtful.—Certain writers are of the opinion that the minerals found in clays and soils do not retain the crystal condition, but pass over to the colloid state when slightly under 0.001 mm. in diameter. If such is the case, it is a sad fallacy to assume, calculate, and give preponderance to the size of crystal grains under 0.001 mm. in diameter. Seger's smallest fraction, 0.01-0, does not unduly exalt this fine matter in the surface factor.

Effect of Size on Physical Properties of Clay Wares.—Clays containing large amounts of residue above 0.04 mm. in size are too coarse for fine pottery. China clays containing considerable amounts of the 0.040-0.025 mm. size are the "safest" used in potting. Most of the commercial English china clays have practically no residues coarser than 0.025 mm., while if they have but slight residues coarser than 0.010 mm., they are exceedingly liable to cause big losses from cracked ware.

Purdy's mechanical analyses of paving brick clays show a general agreement with this conclusion. The coarsest clays made the toughest brick and the finest clays the weakest brick.

The experimental work of this paper was done before our laboratory was transferred from the Technologic Branch of the Geological Survey to the Bureau of Standards.

SUMMARY.

It is inaccurate to express the size of microscopic mineral grains in "diameters," unless the term is carefully defined. The volumes calculated from microscopic measurement require multiplication by correction factors.

The distribution of sizes in any fraction of clay obtained by mechanical analysis may follow several laws; hence, the various formulas proposed for calculating the mean size are all liable to error. A simple empirical correction factor to the arithmetical mean is apparently as accurate as any more elaborate calculation.

Mellor's surface factor, $\frac{6}{s} \left(\frac{W_m}{d_m} + \frac{W_n}{d_n} + \frac{W_o}{d_o} + \dots \right)$, or

Purdy's simpler form, $\left(\frac{W_m}{d_m} + \frac{W_n}{d_n} + \frac{W_o}{d_o} + \dots \right)$,

best represent the results of a mechanical analysis. The surface factors become uncomparable if different size limits are used in calculations for the smallest sizes. It is advocated that Seger's limits—0.04, 0.025, 0.010 and 0 mm.—give results of most value to clay workers.

THE DECOMPOSITION OF CLAYS, AND THE UTILIZATION OF SMELTER AND OTHER SMOKE IN PREPARING SULPHATES FROM CLAYS.

By HARRISON E. ASHLEY.²

Received December 27, 1910.

In Ost's "Technische Chemie," edition of 1890, p. 129, is the statement that at a Silesian smelter the fumes

¹ *Trans. Am. Cer. Soc.*, **11**, 543-547, 489-492 (1909); **12**, 277-293, 441-442, 445, 779-782, 795-799 (1910); U. S. Geol. Survey, *Bull.* **388**, 48-51 (1909).

² Published by permission of the Director of the Bureau of Standards.

were made to extract alum from shale clay. I cannot find the statement in the 1898 edition of Ost, from which the inference is that the process has been abandoned. A post-mortem examination is not usually inspiring, but as we still have smelter and industrial smokes containing considerable percentages of sulphuric acid, and as clays are found everywhere, the subject is likely to be revived at any time. An uneconomic process of a past decade often develops into a profitable industry of the present through the more definite knowledge of the conditions to be met. During the past few years some notable physico-chemical data on the properties of clays that are involved in such a utilization of clays have appeared in publications inaccessible to many of you, and, together with some original data, are summarized in this paper.

Considering their economic importance, the clays are very imperfectly known as to decomposition and other critical points, as indicated by loss of water, heat absorption and evolutions, specific gravity changes, and solubility in acids.

An incorrect notion that the combined water of kaolin is given off in two stages is very prevalent.

Hillebrand¹ described a sample of pure crystal kaolinite (sp. gr. 2.611) and said "None of the water escapes at a temperature of 330° C.; it is therefore probably all basic water..... Frenzel² has described a variety of kaolin (myelin) which loses none of its water until a very high temperature is reached." Purdy and Moore³ said: "The majority of clays are dehydrated completely when subjected to heat at 500-600° C., others not."

The only experimental figures with which we are acquainted, that show the actual losses in weight on heating clays to different temperatures, are those of A. E. Barnes⁴ and W. M. Kennedy,⁵ a pupil of Orton's. The details of these two tests are given in Fig. 1. Purdy and Moore's statement was likely based upon these tests.⁶

Le Chatelier⁷ made some determinations that appear to have been accepted by all French authorities. He heated tests of typical hydrous minerals in a 5-mm. platinum cone opening in a large crucible filled with calcined magnesia and heated by a Forquignon furnace, taking only 10 min. to reach 1000°. He states that variation of the speed had little effect. Our investigations show that whatever the cause, his results were 100 to 150° C. too high. His results on the decomposition of calcium carbonate have been shown in error by a similar amount.⁸

On the basis of the observed retardations and accelerations, Le Chatelier divided the clays into 5 types:

¹ U. S. Geol. Survey, *Bull.* **20**, 98 (1885).

² Naumann-Zirkel, "Mineralogie," 11th Ed., p. 676.

³ *Trans. Am. Cer. Soc.*, **9**, 213 (1907).

⁴ *Clayworker*, **23**, 705 (June, 1895).

⁵ *Trans. Am. Cer. Soc.*, **4**, 152 (1902).

⁶ I have since learned that Ellis Lovejoy published in the *Clayworker*, 1886 or 1887, the loss of weight at the melting points of different metals, and found the decomposition near the melting point of antimony, 624°+.

⁷ *Z. physik. Chemie*, **1**, 396 (1887). *Comptes rendus*, **104**, 1443, 1517.

⁸ Zavriev, *J. chim. phys.*, **7**, 31-57; *Chem. Abs.*, **3**, 1112 (1909).

Allophane, $Al_2O_3 \cdot 2SiO_2 \cdot Aq$. Retardation between 150 and 220°. A sudden acceleration at 1000°.

Halloysite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \cdot Aq$.—Marked retardation ending at 700°. A sudden acceleration at 1000°.

Crystal Kaolin, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.—Decided retardation, ending at 770°. A slight acceleration at 1050°, "due to colloidal clay always present in kaolin."

Pyrophyllite, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$.—Retardation ending at 700°. A doubtful retardation at 850°.

Montmorillonite, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O \cdot Aq$.—A considerable pause at 200°, one less sharp at 770°, a doubtful one at 950°.

He stated that the halloysite group is the most important, including all the sedimentary and most of the "chemical" clays.

with temperature-time coordinates. The following is a summary:

Clay.	End of retardation.	Remarks.
English china clay, No. 1....	573°, 582, 574	
North Carolina kaolin	578	Acceleration at 940°.
No. 1 fire-clay	592	
No. 2 fire-clay	597	
Paving brick shale	583	
English ball clay	581	
Tenn. No. 3 ball clay	583	Acceleration from 900 to 970°.
N. J. saggar clay	612	
Ohio surface clay	595	
Albany, N. Y., slip clay	590	
Illinois joint clay	574	
Another Illinois joint clay	552, 567	
Minn., highly colloidal	574	
N. Dakota, highly colloidal ..	617, 614	Indistinct.

An individual test is shown in Fig. 2.

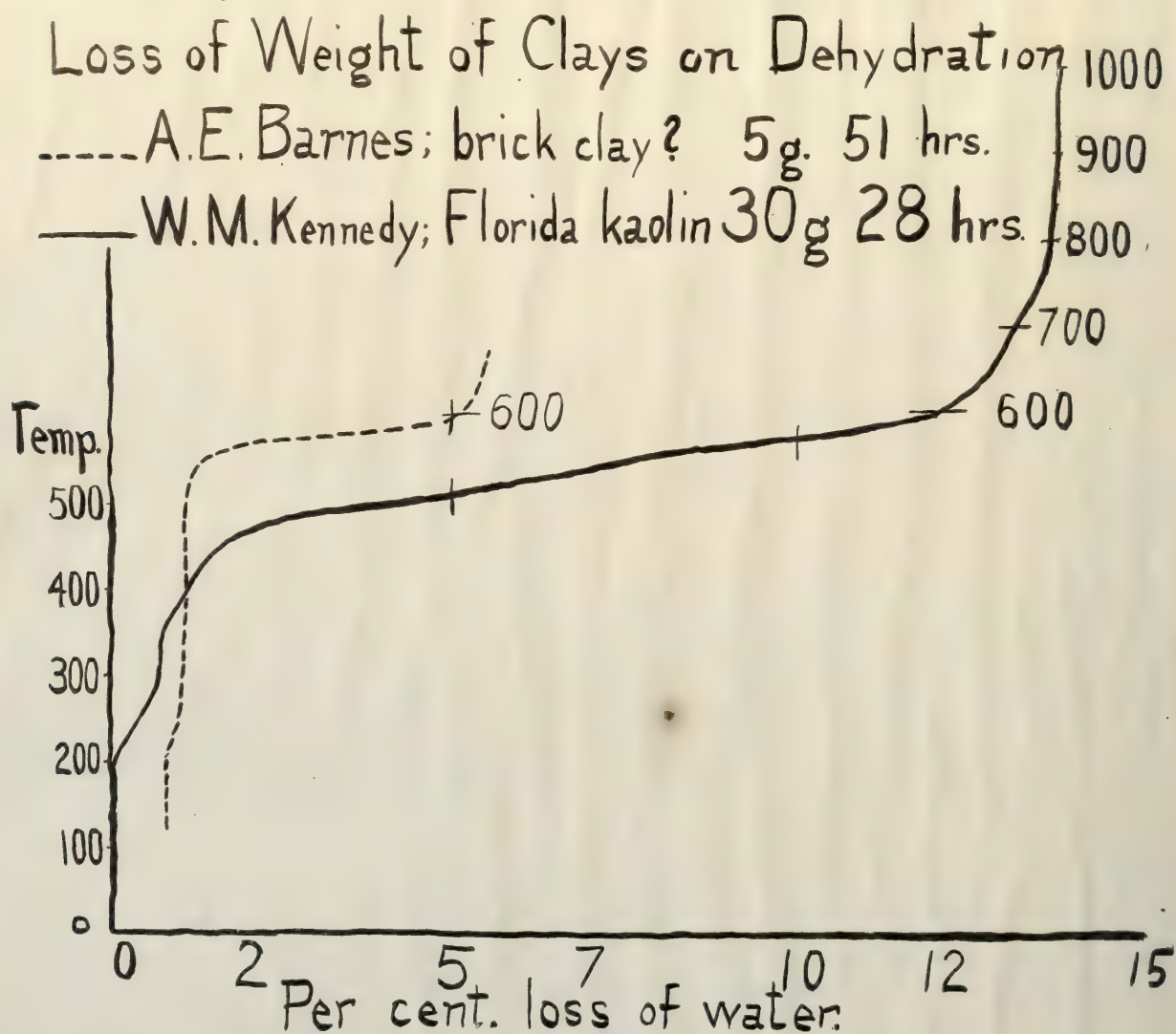


Fig. 1.

We have made only what we consider preliminary tests, heating cylindrical test pieces (5 cm. long, 3.5 cm. in diam., 1 cm. hole half way through the center) in an electric furnace with sufficient current turned on from the start to bring the test-piece to about 1000° in 100 minutes. Usually the runs were carried to 800° only. This gives a very rapid rise for the first few hundred degrees. The results are most readily perceived when put on logarithmic plotting paper

¹ Temperatures as given by Le Chatelier.

An initial slow rate of heating is due to the water held persistently by colloidal clay up to 200 or 300°.

A second retardation from about 500 to 575° is due to the expulsion of all the chemically combined water.

A third retardation from about 825 to 925° is of a wholly unproved nature, possibly the transformation of quartz to tridymite.

The same description, unproved, applies to the acceleration occurring at about 925°, which we suspect

of being due to the formation of sillimanite, a mineral which crystallizes out in clay products at about 1350°C .

The specific gravity determinations of Knoté¹ at the University of Illinois on the same sample of clay confirm our thermal results. Any attempt to

were repeated, except that the retardation at 825 to 925° did not appear with the clay tried (Fig. 3).

In Fig. 4 we have combined the results of Bleining² and Knoté³ on the same clay. The apparent inconsistency of their results is due to the fact that Bleining dried his sample at 100° and Knoté at 115° . Such differences have a profound influence on colloid behavior, as has been noted by Hillebrand, Lord, and others. Knoté made no determinations in the range from 115 to 450° that was studied by Bleining.

With cold reagents the colloid matter of clay is very reactive with dilute reagents (below 0.1 formal), as described by the author,³ but the crystal matter is quite insensitive.

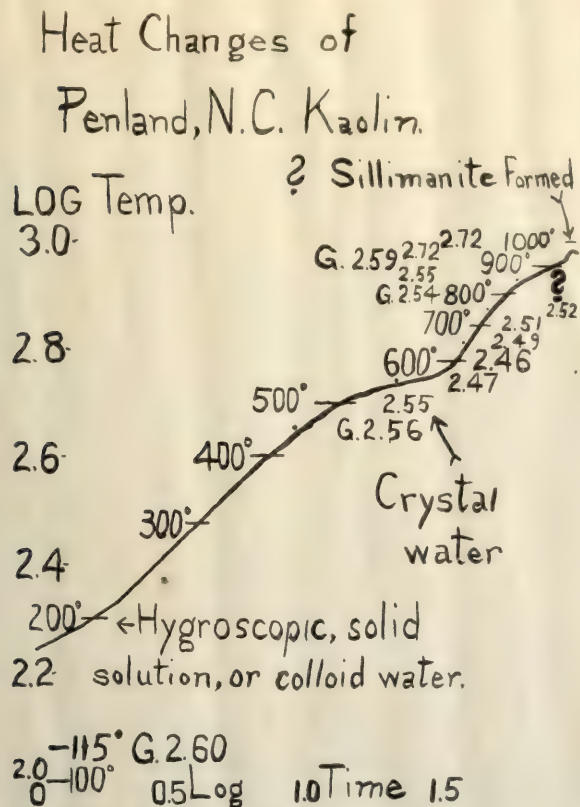


Fig. 2.

determine from the specific gravities of sillimanite (3.2), quartz (2.65), tridymite (2.3), and corundum (4) what compounds exist at 1000° is futile, as the lightest possible mixture has a specific gravity of 2.95, as opposed to Knoté's determination of 2.72.

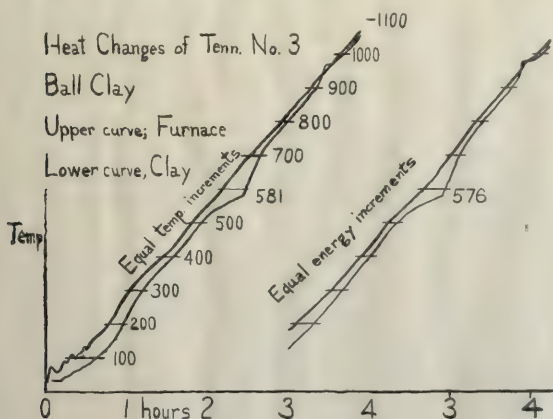


Fig. 3.

We have later tried heating the furnace at a regular rate, and also by equal electrical energy increments. All of the above-mentioned observations

¹ *Trans. Am. Cer. Soc.*, **12**, 226 (1910).

Specific Gravity of Kaolin.

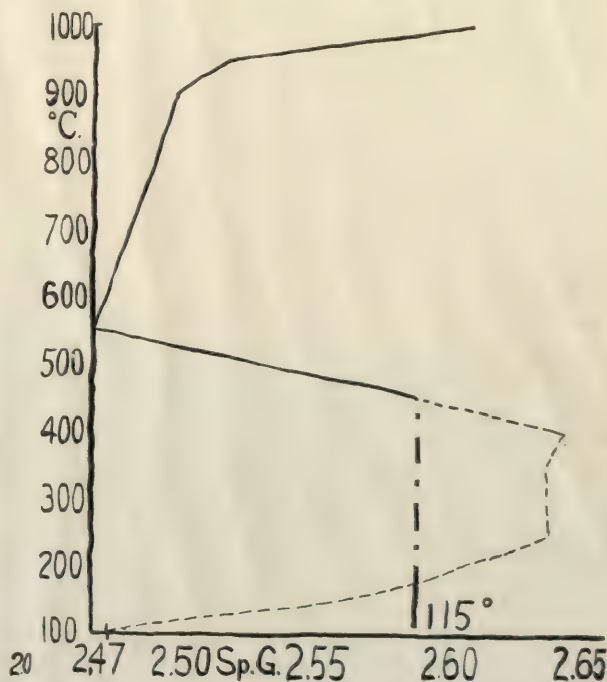


Fig. 4.

Below, say 300° , it is well known that the aluminum of clay is dissolved by hot concentrated sulphuric acid.

According to F. W. Clarke:⁴ "After dehydration at low redness, kaolin is completely decomposable by hydrochloric acid, but the ignited mass contains no silica soluble in sodium carbonate solution." The above data give a more precise temperature limit for the beginning of solubility.

Knoté boiled Olive Hill, Ky., fire-clay with 1:3 hydrochloric acid, followed by treatment with 1 gram NaOH and 3 grams Na_2CO_3 per 50 cc. The results were:

¹ *Trans. Am. Cer. Soc.*, **12**, 504 (1910).

² *Ibid.*, **12**, 226 (1910).

³ *Ibid.*, **12**, 768 (1910).

⁴ U. S. Geol. Survey, *Bull.* **125**, 32.

	Extraction. Per cent.
Raw clay.....	6
Ignited at 600°.....	44
Ignited at 1000°.....	5

Edgar ball clay ignited at 600° gave 70 per cent. extraction, while raw clay and 1000° ignition also gave small extractions.

Le Chatelier stated that the heat evolution at 1000° accompanies the change by which Al_2O_3 becomes insoluble in acids.

Ries¹ found a few tenths of 1 per cent. soluble salts in unburned clay, 4.50 per cent. in soft-burned, and 1.03 per cent. in hard-burned. Evidently the soft-burned clay took up sulphuric acid from the fuel to some extent. At sufficiently high temperatures² silica will displace the sulphuric acid from its compound with alumina.

In this article we have compiled most of the data available, showing at what points changes take place in the chemical nature of clays. The technical application of this data for the purpose of extracting soluble sulphates from clays by smelter smoke is outside the province of the laboratories with which we are connected. As Prof. Bleininger remarked when the writer proposed the title: "There will likely be mighty little about smelter smoke and a lot about clays in your article."

Brick-yards are sometimes much objected to because of the large amount of sulphuric acid they discharge into the atmosphere. In Belgium lime is sometimes put on the kiln tops to capture the acid fumes. It has been noticed that wood on the top of scove or field kilns becomes impregnated with sulphuric acid, and the writer has been questioned by a manufacturer as to whether such condensed acid is finally discharged into the atmosphere.

In a certain large city, where the suppression of acid brick-yard smoke is agitated, and where the brick commonly used are but soft-fired, the amount of soluble salts is unusually large. It is inconceivable that all of these salts were originally in the clay used. Hence it would appear that the brick-makers, probably unintentionally, are delivering sulphates in bricks rather than into the atmosphere.

It appears, then, that any clay ignited between 600 and 900° C. will take up acids quite readily. The methods of utilizing this fact and the economy of processes are not discussed.

The retardation points given on p. 92 were determined under the direction of Prof. A. V. Bleininger by Messrs. R. K. Hursh and S. E. Young. The curves with equal temperature increments and equal energy increments were made by the writer.

EXTENT AND COMPOSITION OF THE INCRUSTATION ON SOME FILTER SANDS.

By E. BARTOW AND C. E. MILLAR.

Received January 7, 1911

When lime is used in connection with water puri-

¹ "Clays of Wisconsin," Wisconsin Survey, *Bull.* 15, 22 (1906).

² H. A. Seger, "Collected Writings," American Ceramic Society Translation, 2, 583, 646 (1902).

fication there is a tendency to form an incrustation in the pipes or on the sand grains of the filters. In some cases the sand grains have become so large that it has been necessary to put in new sand. Cases have been reported where the sand near the bottom of the filters has caked into a solid mass.¹

We have investigated the sand in some filters in Illinois. Samples of sand were sent to us from Danville (2), Kankakee, Quincy, and Moline. We are indebted to H. M. Ely, Danville, C. H. Cobb, Kankakee, W. R. Gelston, Quincy, and to M. Olson, Moline, for information concerning the sand used.

The Danville plant used Red Wing, Minn., sand having an effective size of 0.31 and a uniformity coefficient of 1.8. During periods of low turbidity from 0.27 to 0.7 grain per gallon of lime and from 0.58 to 1.5 grains per gallon of iron sulphate were used. In periods of high turbidity from 0.8 to 2.5 grains per gallon of lime and from 2.5 to 4.0 grains per gallon of iron sulphate were used. Filter No. 8 has been in use 7 years and filter No. 6 5 years. A larger proportion of lime was used prior to the last 15 months.

The Kankakee plant uses Mount Tom sand. The size at the beginning is not known. The sand has been in use 9 years, but only during 1 year has 1 grain per gallon of iron sulphate and 2 grains per gallon of lime been used. During the remainder of the time alum has been the coagulant.

The Quincy plant uses Red Wing, Minn., sand having an effective size of 0.38 and a uniformity coefficient of 2.1. While the sand has been in use a long time, it is not possible to tell the exact time, for about two years ago, the sand was removed from the filters, screened, and the finest replaced. It has undoubtedly been in use more than 7 years, for Quincy was the first plant in the country to use the lime and iron sulphate process. During the last 4 years an average of 2.05 grains per gallon of iron sulphate and 2.84 grains per gallon of lime were used.

The Moline plant has been in operation without removal or change of the sand for five years. Alum has been used about nine months; previous to that, lime and iron sulphate were used regularly, 1 grain per gallon of iron sulphate and 3 grains per gallon of lime being used.

The sand received has been examined to determine the relative amount of the incrustation, the size of the incrustated grains, and the composition of the incrustation.

TABLE I.

Name of sand.	Danville, No. 8.	Danville, No. 6.	Kankakee.	Quincy.	Moline.
Weight of sand taken.	343.0	351.0	383.0	325.0	330.0
Weight of residual sand	232.0	238.0	330.0	49.0	94.0
Weight of incrustation removed.....	112.0	113.0	53.0	276.0	236.0
Per cent. of incrustation.....	32.4	32.2	13.7	84.7	71.4
Per cent. increase by incrustation.....	47.9	47.7	15.9	633.0	249.0

¹ *Eng. and Min. J.* May 6, 1908. Report of Ohio State Board of Health, 1908.

In determining the relative amount of the incrustation, we used approximately 250 cc. of each filter sand, which we carefully weighed and treated with hydrochloric acid until all the carbonate was dissolved. The residue was washed and weighed. The results are shown in Table I.

As the filter sands are of quartz and are unaffected by acids, this treatment gives quite an accurate means of determining the increase. It is hard to realize what an enormous increase these figures imply. An incrustation amounting to 71 per cent. means that there is an increase by weight of 249 per cent., and an incrustation amounting to 84.7 per cent. represents an increase of 633 per cent. With this increase in the size of the grains there has been an equivalent loss of sand, which has been carried into the sewers. The increase in the size of the grains is accompanied by loss of efficiency. As the grains increase in size, the interstices between the grains are larger and fine particles more readily pass through.

The size of the incrustated grains has been determined by the ordinary sieve method. The results are shown in Table II:

TABLE II.

	Effective size.	Coefficient of uniformity.
Danville No. 6.....	0.52	1.30
Danville No. 8.....	0.55	1.50
Kankakee.....	0.61	1.68
Moline.....	0.60	1.90
Quincy.....	0.77	1.67

A sand with an "effective size" above 40 would not be chosen for a filter sand. We can, from the table and by comparison with the original effective size, see that considerable deterioration has taken place. A calculation of the volume of the sand from Quincy before and after the incrustation formed shows a seven-fold increase. This corresponds to the 655 per cent. increase by weight shown by treatment with acid.

The composition of the incrustation was determined by evaporating to dryness a portion of the hydrochloric acid solution and analyzing the residue. The results obtained are shown in Table III:

TABLE III. COMPOSITION OF INCRUSTATION ON FILTER SANDS.

Determinations made.	Danville No. 6.	Danville No. 8.	Kankakee.	Quincy.	Moline.
Insoluble matter.....	5.89	7.58	1.83	0.32	1.20
Oxides of iron and aluminium, $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$	2.20	3.15	7.20	0.42	0.94
Magnesium oxide,..... MgO	1.16	1.00	1.09	0.83	0.12
Calcium oxide,..... CaO	49.58	47.70	47.75	54.03	53.10
Sulphur trioxide,..... SO_3	0.17	0.17	0.31	0.14	0.12
<i>Hypothetical combinations.</i>					
Magnesium sulphate,..... MgSO_4	0.26	0.25	0.48	0.21	0.18
Magnesium carbonate,..... MgCO_3	2.23	1.90	2.00	1.63	1.37
Calcium carbonate,..... CaCO_3	88.53	85.17	85.26	96.48	94.83
Ferrous carbonate,..... FeCO_3	3.19	4.57	10.44	0.61	1.37
Insoluble matter,.....	5.89	7.58	1.83	0.32	1.20
Total.....	100.10	99.47	100.01	99.25	98.95

It will be noticed that calcium carbonate is the predominant substance. This corresponds to the composition of the incrustation found in the pipes at Quincy.¹ The incrustation at Kankakee contains

the smallest proportion of calcium carbonate. This may be due to the composition of the mineral content of the water, or to the fact that lime had not been used for some time before the sample was taken. According to the analyses of the mineral content of the river waters,² the Kankakee river water contains the least carbonate and the greatest amount of sulphate.

The formation of incrustation on the sand grains is due to incomplete precipitation of calcium carbonate before the water reaches the filters. While the greater part of the calcium carbonate is precipitated quickly an appreciable quantity remains at the end of six hours. The precipitation will take place more rapidly if the water is agitated. The after-precipitation on the sand grains may be prevented by increased sedimentation, which often cannot be done because of the expense, by agitation of the treated water or by the addition of carbon dioxide. The carbon dioxide can be added directly or can be made by the addition of iron sulphate or aluminium sulphate. Carbon dioxide has been successfully used at Winnipeg. It was prepared by burning coke in the furnace used to run the filter machinery.

Sulphate of iron is being used in some of the newer installation as at New Orleans,³ where the iron is added after the lime and where the water treated with lime is thoroughly agitated.

The reactions with the sulphates of iron and aluminium are double, for both calcium sulphate and calcium acid carbonate are formed. Neither of these substances will form an incrustation on the sand grains.

Laboratory experiments along the above lines indicate that the action of the iron and aluminium sulphates, following lime, is immediate, so that very little time need be allowed between its addition and the application of the water to the filters.

Experiments with carbon dioxide, either pure or as found in purified flue gases, show that there is a removal of the incrustation; blank experiments with air showed no removal. The substitution of purified flue gases for the air now so generally used in washing filters would probably prevent the formation of

an incrustation.

ILLINOIS STATE WATER SURVEY,
URBANA, ILL.

¹ U. S. G. S. Water Supply, Paper 239, p. 89.

² Eng. Rec. Apr. 23, 1910. Eng. and Min. J., May 6, 1908.

³ Proc. Am. W. W. Assn., 1908, 172. Univ. of Ill., Water Survey Series, Bull. 7, 35.

ADDRESSES.

THE WORK OF THE CHEMICAL LABORATORIES OF THE BUREAU OF MINES.¹

By J. K. CLEMENT.

The organization of the chemical laboratories of the Bureau of Mines is perhaps unique, in that there is no chief chemist. The work is divided among a number of separate laboratories, each carrying on its own lines of work, under the direction of its own chief—the whole forming a group of more or less independent units. The relation of the work of the several chemical laboratories to that of the other departments of the Bureau varies with individual cases. In general, however, the problems of the chemists are closely connected with those of the mining and mechanical engineers.

Fuel-Testing Laboratory.—The oldest of the chemical laboratories of the Bureau is the Fuels Laboratory, which was established in connection with the fuel testing plant at the St. Louis Exposition in 1904. This laboratory, which is in charge of Mr. A. C. Fieldner, is occupied mainly with the analysis and calorimetric testing of fuels, including coal, coke, lignite and peat.

The samples submitted for analysis originate not only in the various sections of the fuel-testing and mine investigation divisions of the Bureau of Mines, but also in the various bureaus and departments of the Federal government. In addition to analyzing samples of all fuels used in the boiler and gas producer tests, ultimate analyses and calorific value determinations are made on mine samples of coal collected by the U. S. Geological Survey, as well as by certain state geological surveys. The data of these latter tests are of value in establishing the composition and heating value of the coals in connection with the classification of the coal fields of the United States.

A bulletin, now in course of preparation, gives the analyses and field data of all mine samples—about 5000—of coal tested since the establishment of the Government Fuel Testing Plant at St. Louis.

In addition to the laboratory at Pittsburg, there is located in Washington, D. C., a laboratory in which are tested samples of coal delivered to the various buildings, arsenals, navy yards and military posts within the District of Columbia, and in various ports of the country and of the coal purchased by the Panama railroad.

Fusibility and Clinkering of Coal Ash.—In the use of coal under steam boilers, the property next in importance to its calorific value is perhaps the amount and fusibility of its ash. Indeed, some coals, which have a high heating value, are practically worthless for making steam on account of their tendency to clinker and adhere to the grate bars. The clinkering property of coal seems to be a function not only of the ultimate composition of the ash, but also of the character of the minerals from which the ash is formed.

Mr. F. M. Stanton is now engaged in an investiga-

¹ Read before the Minneapolis meeting of the American Chemical Society. By permission of the Director of the U. S. Bureau of Mines.

tion of the relation between the fusibility and clinkering properties of coal ash and its chemical and mineralogical composition. Analyses already made indicate that the composition of clinkers obtained from different boiler tests with the same coal is constant, and that the composition of the clinker is more uniform than that of the ash itself.

It is interesting to note that TiO_2 was found in all the clinkers examined in amounts varying from 1 to 3 per cent. Determinations of the fusion point of various ashes give values ranging from 1150° to 1400°C .

Chemistry of Petroleum Technology.—Although the U. S. Geological Survey has issued a number of bulletins of a geological and statistical nature concerning the more important petroleum districts of the United States, until quite recently there has been practically no authentic or comprehensive information concerning the technical value of American petroleum available in scientific literature. Realizing the urgent need of such information, in 1907 the Technologic Branch of the Geological Survey began the systematic study of the commercial bodies contained in the crude petroleum of the United States, of the methods for their separation and purification and of their economic use. The California fields, because they gave at this time the greater promise of a large and continued production, and because of their proximity to naval stations, and the peculiar adaptability of the product as a maritime and locomotive fuel, have been selected for first study.

The following publications concerning this work are now in course of preparation by the Bureau of Mines:

A bulletin on the "Physical and Chemical Properties of the Petroleum of the San Joaquin Valley Oil Districts of California," including analyses of some 180 samples of petroleum from this valley, with a chapter on "Natural-Oil Gases" and with detailed descriptions of the methods of analysis employed in the Bureau of Mines laboratory.

A circular on "Methods of Sampling Petroleum and Oil Gases with Specifications for Fuel Oils."

A bulletin concerning "The Technology of Petroleum of the United States," showing the necessary steps and approximate costs of acquiring petroleum-bearing lands, their development and the technical handling of the oil and its disposal.

A "Chemico-geological Brochure of Petroleum," endeavoring to show the relations existing between the chemical-physical properties of the petroleum from the Coalinga and Midway-Sunset fields of California and its geological location.

Among the problems in which this laboratory is occupied are the following:

The determination of the specific gravity of petroleum, with special attention to variations of specific gravity with change in temperature.

The determination of the viscosity of crude petroleum and the factors governing its rate of flow through pipes.

The separation of water contained in the crude

petroleum by centrifuging, distillation, electrical treatment, and treatment with carbides.

The relation between the flash- and burning- points, and their significance.

The accurate determination of calorific value.

A study of the various processes of distillation, both on a laboratory and commercial scale.

An investigation of the methods of refining from an economic standpoint.

An investigation of the properties and uses of the various refined products of petroleum.

These and corollary problems are conducted primarily as a scientific study of the technology of the resources of the United States, and also to ascertain fixed properties and values, in order that the various government departments may be better able to make their purchases of petroleum products. These petroleum investigations are in charge of Mr. Irving C. Allen.

Combustion Investigations.—The work of the Fuel Testing Plant at St. Louis demonstrated the desirability of an investigation of the fundamental principles underlying the combustion of coal in boiler furnaces and in gas producers. Mr. J. C. W. Frazer, Mr. C. E. Augustine and the author are charged with an investigation of the processes of combustion and the conditions requisite for complete combustion, with coals varying in the content of volatile matter, with various rates of firing, various rates of heating of coal, and with variations in the amount of air supply, and in the rate of mixing of air with the volatile combustible. The work is being carried out in a furnace especially designed for the purpose, and having an unusually long combustion chamber. A single test involves the taking of about 35 gas samples simultaneously.

The author, with Mr. L. H. Adams, has completed an investigation of the rate of formation of carbon monoxide from carbon dioxide and carbon, and the rate of formation of water gas, at high temperatures. The results, which will appear in a forthcoming bulletin, No. 7, of the Bureau of Mines, show that the velocities of these reactions increase rapidly with rise in temperature, and that by operating gas producers at higher temperatures than is customary in present practice, a large increase in capacity should be obtained.

A special gas producer has been constructed for investigating the processes of producer gas formation, and an attempt will be made to apply the results of the laboratory tests on a commercial scale. The operations are in charge of Mr. C. D. Smith, mechanical engineer, Dr. Frazer and the author.

The Composition of Coal.—In connection with the chemical investigations undertaken by the Bureau of Mines, it was realized that the amount of information available relating to the chemical composition of coal was small in view of the importance of the subject. Our scientific knowledge of the chemical character of coal is limited almost entirely to its chemical analysis and its adaptation to certain industrial operations. It was considered by this bureau a matter of sufficient

importance to justify the initiation of investigations having for their object the isolation and identification of some of the constituents of coal. So far the efforts in this work have been confined to such treatment of the coal as will not affect the composition of any of the constituents.

By the use of inert solvents, it is possible to extract as much as 35 per cent. of the original coal. By the subsequent use of neutral solvents and by fractional distillation in a vacuum, it has been possible to isolate a number of different substances. Some of these are oils, others solids varying in color from light yellow to dark brown. The analyses and molecular weights of some of these substances have been determined, and in a few cases it is believed the materials are practically pure substances.

This work is being continued on a larger scale than heretofore, in order to obtain greater amounts of the various fractions separated from the crude extract which is obtained from the coal, and it is hoped that results of a definite character will be forthcoming. Dr. E. J. Hoffman is associated with Dr. Frazer in the execution of this investigation.

The Volatile Matter of Coal.—Closely related to the boiler and gas producer tests of the Bureau of Mines, as well as to its investigation of the manufacture of coke, is the investigation of "The Volatile Matter of Coal," the results of which have been recently published in a Bureau of Mines bulletin, No. 1, by H. C. Porter and F. K. Ovitz. These authors have determined the quantity and composition of the gases evolved from various coals when heated to temperatures varying from 400° to 1000° C.

Further experiments along this line are now in progress, and particular attention will be given to the influence of the rate of heating on the character of the gases produced, to the initial composition of the gases at the instant of liberation, and to the thermal decomposition of these gases during passage over heated surfaces.

Weathering and Deterioration of Coal.—Under the direction of Dr. H. C. Porter, a series of tests is being carried on by the Bureau of Mines, in cooperation with the Navy Department, on the deterioration of coal in storage, with special reference to storage by submergence in sea water. The coal used in these tests is from the New River, W. Va., district. Analyses already made show that the coal stored in sea water and in fresh water has not deteriorated appreciably in the heat value of its fuel substance; and further, that the coal stored in the open air, under unusually adverse weathering conditions, has not lost in any case more than 1.0 per cent. of its heat value in one year. Similar tests, with Pocahontas coal, are in progress on the Isthmus of Panama, in cooperation with the Panama Railroad Company, the coal being stored in a 120-ton pile in the open air; and on Pittsburgh coal, in cooperation with the University of Michigan, in which deterioration in gas-making qualities, as well as in heating value, is being investigated. Weathering tests on sub-bituminous coal have been made at Sheridan, Wyoming.

A forthcoming circular of the Bureau of Mines, entitled "The Accumulation of Gas from Coal," will present results which show the quantity and rate of formation of inflammable gas from freshly mined coal at ordinary temperature, and the rate of absorption of oxygen by the coal.

The Burning of Coal in Mines under Diminished Supply of Oxygen.—Another problem in which an appeal for aid has been made to the chemist is the combatting of mine fires. Dr. Porter has begun an investigation of some of the factors on which depends the propagation or extinguishing of fires in mines, especially the effect of variations in temperature and in the oxygen content of the surrounding atmosphere on the progress of combustion and on reignition.

Examination of Mine Gases.—One of the laboratories of the Bureau is devoted to the study of mine gases. An extensive investigation of the subject is being made on samples collected under all possible conditions—from normal mine air, from the after-damp following mine explosions, from stagnant areas and from burning areas during mine fires, and from the gases produced by blasting explosives. These investigations are in charge of Mr. G. A. Burrell.

A new apparatus has been devised for the determination of small amounts of CO in gas mixtures by the iodic acid method.

Samples of gas, taken from burning areas, during the progress of mine fires, have been examined, with a view to gaining more complete knowledge of the chemical processes involved. By means of a specially devised portable apparatus, samples have been analyzed immediately after being taken, and valuable information furnished to those engaged in fighting the fire.

The effect of fluctuations in barometric pressure on the exudation of methane in mines is being investigated. The methods and apparatus used in the examination of mine air will be described in a forthcoming bulletin.

Influence of CO₂ on the Explosibility of Mine Gases.—The blanketing effect of carbon dioxide on the explosibility of gas mixtures is being investigated in one of the laboratories of the Bureau. The results show that the presence of this gas reduces considerably the range of explosibility of mine gas.

The Chemistry of Explosives.—The Explosives Laboratory, under Dr. W. O. Snelling, is occupied with (1) the analysis of all explosives submitted to the Bureau by manufacturers for test, and with such tests as are necessary to determine the stability of these explosives under different conditions of temperature, and the liability of the explosive to exudation; (2) the chemical analysis of the products of combustion of the above explosives obtained after explosion in the Bichel gauge; (3) the chemical analysis of electric detonators, blasting caps, fuses, etc., used in connection with the physical tests on explosives.

Among the research problems with which the laboratory is engaged are the following:

A study of a chemical method of determining the relative strength of electric detonators, blasting caps, etc., by means of the decomposition produced in a practically non-explosive body capable of undergoing decomposition under the influence of a strong detonating shock.

The development of a method of determining the relative strength of electric detonators, blasting caps, etc., depending upon the degree of pulverization of sand or other suitable material which is effected under fixed conditions by the force of the detonator or blasting cap.

Investigation of a method for determining the relative liability of nitroglycerine explosives to exudation, and of measuring the ability of different explosives to retain absorbed constituents.

An extensive investigation of methods of analysis of explosives. Considerable work has already been carried out toward the preparation of a bulletin on this subject.

In addition to the above work, this laboratory is engaged in the inspection of all explosives, including dynamite, blasting caps, electric detonators, fuses, etc., purchased by the Isthmian Canal Commission. This work includes the analysis of such explosives and tests to determine their safety during transportation. Daily analyses are made, at the works of the manufacturers, by one of the chemists of this laboratory, covering all dynamite purchases for the use of the Isthmian Canal Commission, and tests of other materials made at each inspection period. To illustrate the extent of this inspection work, it is noted that there were made during the fiscal year, ending July 1, 1910, 434 analyses of dynamite, 69 analyses of electric detonators, and 2279 physical tests of electric detonators.

Coal Dust Explosions.—Some of the most important and most difficult of the problems confronting the mining engineer relate to the safety precautions necessary to mitigate the dangers encountered in coal mining operations. The two greatest sources of danger to be combatted here are the explosive gases given off by the coal, and the finely divided coal dust which exists throughout most coal mines. The first danger can be overcome only by increasing the ventilation in the mines. Unfortunately, this increases the danger from the coal dust by the removal of its moisture. The coal dust problem has greatly interested mining engineers recently, and is now being investigated by nearly all coal mining countries, and a great deal of attention has been given to the subject by the Bureau of Mines.

The greatest danger from coal dust, in the absence of mine gases, is in connection with the use of explosives, as the ignition of coal dust from other sources is not so likely to occur. The first efforts of the Bureau of Mines, therefore, has been, by systematic tests, to determine those explosives which are least liable to cause the ignition of explosive gases and coal dust. This work has resulted in the preparation of a list of explosives known as "permissible explo-

sives," which, when properly used, will minimize the danger from this source.

In this connection, efforts have been made to devise a laboratory method to test the inflammable character of samples of coal dust, and to classify them according to their inflammability. This method is based on determining the amount of combustion which takes place when clouds of dust of the same density are ignited under the same conditions, the amount of combustion being determined by the pressure developed within the explosion vessel. In this way it is possible to obtain results on any one sample of coal dust which agree to 3-5 per cent. of the total pressure developed. By varying the temperature of the platinum coil, used as the source of ignition, it is also possible to study the change in the amount of combustion taking place when the source of ignition varies. The result has been to show that when a highly inflammable dust is under investigation, the pressure developed soon reaches a maximum, and an increase of the temperature of the coil causes but little increase in the pressure developed, indicating that the combustion has propagated throughout practically the whole cloud of dust. With a slightly inflammable coal dust the pressure developed continues to increase with increasing temperature of the coil over the whole range of temperature at which it is practicable to operate.

One of the proposed means of lessening the inflammable character of coal dust is to add a non-inflammable dust. The laboratory method used to investigate the inflammability of coal dust has been extended to various percentages of coal dust and finely ground shale in order to determine to what extent the combustion is limited by the presence of the inert dust. The experiments indicate that a marked diminution of pressure is not obtained until about 25 per cent. of inert dust is added, the pressure then falling off rapidly with a further increase in the amount of shale dust added. This investigation is in charge of Dr. J. C. W. Frazer.

DISPOSAL OF STARCH FACTORY WASTES.¹

By T. B. WAGNER.

When your esteemed President asked me, about two months ago, to read a paper before this meeting, I accepted his invitation with much hesitation, not only because of pressure of business, but particularly because I do not consider myself well qualified to speak on such subjects as come up before your Association. While I desire to make my remarks as brief as possible, I believe that I shall have to go back into the history of the industry of corn products, to give you a better understanding of the subject under discussion.

In the early stages of the corn products industry, that is, primarily the manufacture of corn starch, dating back fifty years or more, the manufacturers concerned themselves solely with the starch contained in the corn; the other constituents of the corn were to them of no concern. These constituents are, the

outer hull of the corn—the so-called bran—the gluten located immediately underneath it, and finally, the germ of the kernel itself. When you consider that corn contains approximately 10 per cent. of nitrogenous matter, you will note that in a small factory consuming only about one thousand bushels of corn a day, this ingredient alone would amount to approximately 5600 pounds per day. The bran forms about the same percentage of the corn and there would be a like waste from this source. However, there are no starch factories operating on so small a scale to-day, the smallest consuming about five thousand bushels a day, whereas the larger factories, which usually produce not only starch but glucose and sugars as well, grind about twenty-five thousand bushels a day. Our Argo factory represents the latest achievement in the corn products industry and its grind, a year from now, will approximate fifty thousand bushels a day. I give you these figures so that you may fully appreciate the importance of the recovery of the by-products. If these by-products were not recovered, our industry could not exist, not only for financial reasons, but particularly because the waste of the by-products would lead to intolerable conditions from a sanitary point of view. Our industry has made remarkable progress. At the time the above conditions prevailed, that is, when starch factories did not recover any by-products, the total recovery of the corn did not amount to more than 50 per cent.; that is to say, all that a manufacturer produced from a bushel of corn weighing 56 pounds were about 28 pounds of commercial starch, part of the starch and all other ingredients of the corn going to waste.

With the introduction of the recovery of the by-products, this yield was, of course, greatly increased until it finally reached about 92 per cent. Only about ten years ago this was considered a good showing for any starch or glucose factory. With the construction of modern plants and the introduction of modern machinery, and through the closest attention of the operating men to the smallest details of the process, it was possible to increase this yield to 95 per cent., which as recently as four years ago, was considered a most excellent result. Since then, the yield has been further increased so that the new standard is 98 per cent., although we have had months where some of our factories recovered as much as 99 $\frac{1}{2}$ per cent. You will note from this that the trade waste from a modern starch or glucose factory cannot be considerable, expressed in per cent., yet it reaches large proportions when applied to the corn consumed. Mr. Sjoström will give you the exact figures as to the amount of this waste.

When we undertook to treat our trade waste at our Waukegan factory, it was not done for the purpose of recovering this waste, but our efforts were the result of an action taken by a number of residents of the town of Lake Forest, located on Lake Michigan, eight miles south of Waukegan. These parties claimed that our trade waste was carried in the waters of Lake Michigan and while in transit became putrefied and created obnoxious odors which made life very un-

¹ An address delivered before the Lake Michigan Water Commission, Chicago, December 17, 1910.

pleasant for them. They brought an action in the Federal Courts, for the purpose of having the Warner Sugar Refining Company (the predecessor of the Corn Products Refining Company) either instal the necessary apparatus and process to remedy the trouble, or cease operating the factory. The principal factor in producing the trouble was the steep-water; that is, the water in which the corn is soaked and which contains by far the largest amount of the soluble ingredients of the corn. At the time the suit was brought this steep-water amounted to 200,000 gallons a day. While this suit was pending, the Corn Products Company succeeded the Warner Sugar Refining Company, and the first step it took was to instal the necessary evaporating apparatus to recover this water in the same fashion as is the practice in its other factories. This relieved the situation very much. Upon investigation, however, we found that the remaining waste was discharged into the lake immediately at the shore and that there was no means of diluting this trade waste, which was carried in concentrated form, so to speak, southward toward Lake Forest. We, therefore, laid a new sewer pipe, about thirty inches in diameter, and carried it into the lake a distance of two thousand feet; at this point the lake is about fourteen feet deep, and it stands to reason that with the current usually existing in Lake Michigan, we secured an enormous dilution of these waste waters. While a great improvement was made in this way, the conditions still remained unsatisfactory. This was because the waste waters contained a not inconsiderable amount of suspended matter which cannot be recovered or isolated by filter presses or other means usually employed for such purpose. Mechanical means being unsuccessful, our only hope lay in a chemical treatment, the governing thought being that if we employed a precipitant, such as lime, this finely suspended matter might be thrown down together with the precipitate formed by the action of the lime. The results obtained in experiments conducted on a small scale were so complete and surprising as to tempt one to consider this theory an inspired one. It is remarkable how completely this suspended matter is thrown down and how quickly the precipitate settles to the bottom.

Filter presses being out of the question, the success of this scheme depended upon the rapidity with which this precipitate would form and how clear the supernatant water was. The tests were carried out in a large tank with cone-shaped bottom, holding about 28,000 gallons of water. The results were highly satisfactory; immediately after the addition of the lime the precipitate settled to the bottom and the supernatant water was as clear as spring water. A series of tests were then made with the treated water, with the particular view of ascertaining how quickly the dissolved oxygen would oxidize the organic matter. The large amount of dissolved oxygen in Lake Michigan water and the enormous dilution secured by our method of discharge brought about this result in a very satisfactory manner. I shall not go any further into the details of this process, as Mr. Sjostrom will deal with that in his talk.

We do not claim that we have solved the problem of the proper treatment of trade waste from starch and glucose factories, but we believe that we have gone as far as we can go with the present knowledge of the subject. I think we are the first ones, so far as our industry is concerned, who have ever undertaken to treat waste waters on so large a scale as is being done at Waukegan. The undertaking was not a small one and involved a very large expenditure of money. I do not believe that a mechanical or chemical treatment will ever yield a trade waste free from objections. The ultimate solution must come from within the factories; that is to say, we shall keep on devising ways and means of recovering in the factory all the soluble matter still discharged in our waste waters, and while it may take years to accomplish this end, I believe that eventually we shall be successful.

CORN PRODUCTS CO., CHICAGO.

TREATMENT OF WASTE WATER FROM A STARCH AND GLUCOSE FACTORY.¹

By OTTO A. SJOSTROM.

The waste water from a starch and glucose plant is composed of effluents from different departments of the factory. In speaking of the components of the discharge through the main sewer we distinguish between condenser-water, gluten cones overflow-water, starch cones overflow-water, and feedpress-water.

Of these the condenser-water represents by far the largest amount but can be left out of consideration in this connection, as it does not contain any products from the manufacture. It happens occasionally, of course, that the vacuum pans entrain soluble solids so that some sugar is lost with the condenser-water. As this is a serious but avoidable loss, due to irregularity of the machinery, a close watch is always kept on this water and whenever tests indicate traces of sugar steps are immediately taken to remedy the trouble.

The different names of the other effluents do not indicate that the composition of the solid matter is different. A short outline of the method of manufacture will give a better understanding of the nature of the waste.

The corn is first steeped for some time with water, slightly acidulated with sulphurous acid. This softens the corn thoroughly and prepares it for grinding. The corn is first ground coarse and passed through machines for removing the germ. It is then ground very fine in stone mills. The so-called mill slop issuing from the mills is run over shakers and reels in order to separate the starch and gluten from the hulls. The hulls are washed to make this operation complete. The starch milk is run over the so-called tables, where the starch settles. The gluten is lighter and remains suspended in the water which tails over the end of the tables. This gluten milk is then run into settlers, which are built with a conical bottom. The operation of settling is continuous. The bulk of the

¹ Corn Products Refining Co.'s Plant at Waukegan, Ill. An address read before Lake Michigan Water Commission, Chicago, December, 1910.

water overflows at the top and this is what we call the gluten cones overflow-water. The concentrated gluten milk which is drawn continuously from the bottom of the settlers is mixed with the hulls and this mixture is filter-pressed. The water from these presses, the feedpress-water, is evidently the same water as the overflow-water from the gluten cones. The starch milk, which results from the washing of the hulls, is not concentrated enough to be run over the tables. It is therefore run into settlers similar to the gluten settlers. The water overflowing from the top is the starch cones overflow-water.

These waste waters contain the soluble substances in the corn. The larger part of the solubles in the corn, however, is contained in the steep-water, which is obtained from the steeping of the corn, as mentioned above. As the steep-water is drawn from the corn it contains between 6 and 9 lbs. of solids per 100 lbs. of water. It is evaporated to what we call heavy steep-water, with a gravity of 16 to 20° Bé., and mixed with the cake from the presses mentioned above. This mixture is dried and forms a so-called commercial feed, an important by-product of the manufacture.

From these short hints about the manufacture it is easy to understand that the waste waters are practically nothing but extremely diluted steep-water. This dilution prevents, of course, all efforts to utilize the waste waters by concentrating them.

The amount of waste water varies considerably for the different plants, depending upon variations in the manufacturing process. In Waukegan, measurements have been made on several occasions. The first measurements, mentioned by Prof. Bartow, in his report No. 6 of the Illinois State Water Survey, were made by means of weirs and gave too low results, as we found later when we could use in making measurements the large tanks erected for treatment of the water. The discharge of overflow-water from the starch cones is about 1,000,000 gals.; the combined feed-press water and overflow-water from the gluten cones is about 650,000 gals., all in 24 hours. Including the condenser water, the total discharge from the plant is probably about 4,000,000 gals. daily.

The overflow-water from the starch cones contains about 180 grains per gallon dissolved matters. The gluten cones overflow- and the feedpress-water contain about 0.3 per cent., the gluten water about 0.4 per cent. dissolved matter. Obviously it is an impossibility to concentrate these waters economically.

The soluble matter contains about 50 per cent. nitrogenous matters, from 30 to 35 per cent. carbohydrates, and from 15 to 20 per cent. inorganic matters. A varying proportion of the nitrogen is present in the form of amides and amido acids. The inorganic content is mainly potassium magnesium phosphate.

In addition to the soluble matter the waste waters also carry a definite, though much smaller amount of insoluble matter, which consists of starch and gluten, suspended in the water. As the gluten does not settle as well as the starch the gluten overflow-water always contains more, say 25 grains per gallon. The

starch overflow-water contains about 15 grains per gallon. The loss from this source represents about 0.35 per cent. of the corn, or about 2 tons of starch and gluten carried into the lake every day. Compared to the grind, 25,000 bushels per day, the amount of the loss is of course not considerable; but it is evident, that in case of irregularities in the run of the settlers, considerable quantities could occasionally escape to the sewer. A close control is therefore kept of the work of the settlers, and samples are taken and tested regularly many times during the day and night.

It is evident that waste waters like these, containing carbohydrates, proteins and other nitrogenous matters, furnish an excellent material for the fermenting action of organisms like yeast, moulds and bacteria. Microscopic examination of the waters discloses the abundance of these organisms. During the manufacturing process, however, their action is checked or retarded by the presence of sulphurous acid which, as is well known, even in small quantities, is a most efficient poison to microorganisms. The fermentation inside of the plant is in fact limited to the formation of a small amount of lactic acid. Upon emerging from the plant the waste waters contain on an average 0.03 per cent. of sulphurous acid, which amount is too small to prevent fermentation, if the discharged waste is left undiluted.

To our best knowledge, however, the trouble which we have tried to obviate by installing the purification plant is caused, not by the soluble matters, but by the presence of the comparatively small amount of suspended matters. As for the soluble solids, the effluents are carried away by the ever-present currents in the lake and become soon so diluted, and consequently the dissolved matters so widely distributed, that the effect of fermentation or chemical changes, which take place sooner or later, is lessened or not noticeable in the large body of water.

With the suspended solids conditions are different. If they drift shorewards under the influence of certain currents and are deposited along the shore, they may without doubt become offensive. They form an excellent medium for the growth of molds and bacteria and their decomposition is accompanied by the formation of foul-smelling compounds and gases.

More likely this decomposition along the shore is exceptional. As a rule it takes place too far out to become offensive. However, as complaints from residents on the North shore seemed to be supported by observations made by Prof. Bartow and his assistants—these observations are embodied in the State Water Supply Report referred to above—the company decided to act upon and follow the suggestion of Dr. T. B. Wagner in regard to a treatment of the waste water. Dr. Wagner had previously found from experiments on a small scale that the treatment with sulphate of iron and lime was the one best suited to conditions. Money was appropriated and experiments started on a fairly large scale. These experiments led to the erection, in 1907 and 1908, of a plant capable of treating 1,300,000 to 1,400,000 thousand gal-

lons daily. It was not considered necessary to build the plant larger, because in the meantime the superintendent of the plant, Mr. Lenders, had found a way of utilizing part of the waste water over again in the manufacture.

The treating plant thus erected is simple in its arrangement but represents nevertheless an outlay of money of about \$100,000. When it comes to handling such quantities of water within a limited space the apparatus required becomes very expensive, even if the operations are simple.

Before describing the arrangement of the plant I will first give some consideration to the chemical end and to manufacturing data.

It is well known that the iron hydrate formed by bringing together sulphate of iron and lime acts as a precipitant and, being flocculent, carries down with it all suspended matters including yeast, mold and—more or less completely—also the bacteria. In our case we happen to have in the soluble matter an amount of phosphates sufficient to furnish a precipitant in the form of lime phosphate upon addition of the lime. It is therefore not necessary to add any iron sulphate, although we have at times used this salt. The iron acts in the form of iron phosphate, which is of course a good precipitant.

Dr. Wagner found, from experiments on a small scale, that while a small amount of lime was sufficient to precipitate the suspended matters it was necessary to add a large surplus of lime in order to obtain a precipitation, which would be quick enough to allow the handling of the quantities in question without using apparatus of undue size and occupying space beyond what was available. He fixed the amount at 2 lbs. of lime per 1000 lbs. of water. We found later, when working on a large scale, that this amount could be cut down to about 1.4 lbs. per 1000 lbs., or 11.7 lbs. per 1000 gals. In case of less grind and consequent slower run of the settlers this amount can be cut down somewhat but not much, if we expect the water to run clear from the settlers.

This is a very large quantity compared to the amounts added in clarifying municipal water supplies. But as it was out of the question to use large settling tanks and this way of working allows the use of continuous settlers and consequent rapid removal of the sludge, there could be no hesitation as to the method to choose.

The chemical action of the lime is practically limited to the neutralization of the acids and the formation of lime phosphate. Only part of the phosphoric acid in solution reacts with the lime; the rest remains in solution as double salts and in organic combination. At the same time the reaction of the water becomes of course alkaline. A small amount of ammonia is set free from the easily decomposed amides, but otherwise the nitrogenous matters are not affected, or it is at any rate not possible to express the effect chemically. Upon the suggestion of Prof. Bartow we made a series of tests on the changes in dissolved oxygen and in oxygen-consuming power of untreated and treated water, undiluted and in varying dilutions.

Prof. Bartow has discussed the results in the Report mentioned above. The figures indicate that the water is less putrescible after the treatment.

It is evident that if a removal of dissolved organic matters were required from the sanitary point of view, very little would be gained through this treatment. But, as said before, the trouble which has given rise to complaints lies with the suspended solids. These are completely carried down with the precipitate. In addition, the micro-organisms present are also, so to say, wrapped up in and carried down with the flocculent precipitate. The waste water is consequently practically sterile after treatment. This is a distinct point in favor of the treatment. Conditions may occasionally prevail in the lake, which minimize the action of the currents, so that the effluents are, so to say, held together in the lake and only slowly become diluted. In such a case fermentation would soon set in, started by the organisms abundant in the effluents. With these organisms removed through the treatment the danger of any troublesome consequences arising from such conditions is—to say the least—very considerably reduced.

Turning to manufacturing data, the proposition handled is the treatment of about 1,300,000 gals. of waste water in 24 hours. At a rate of 11.7 lbs. of lime to 1000 gals. there are required about 7.5 tons of lime daily. The amount of precipitate obtained is between 8 and 9 tons, figured as dry. Of this precipitate the organic matters—that is, starch and gluten—form about 25 per cent. The precipitate contains from 4 to 6 per cent. nitrogen figured as protein. There are from 5 to 8 per cent. of phosphoric acid in the precipitate. The fact that a large part of the lime acts only mechanically and is recovered as hydrate in the sludge naturally led to experiments in using the sludge over again for precipitating. But all efforts in this direction were futile. We could not get the required almost instantaneous settling with anything but pure lime.

The mechanical arrangement of the treating plant is very simple. The overflow-water is pumped up to the third floor of the plant, where the mixing tanks are located. In the first arrangement we had 5 tanks provided with agitators, each of about 3500 gals. capacity. On top of these tanks were small tanks for the lime, which is made up for use into a milk of about 12° Bé. gravity. The idea was to fill these tanks in succession, run in the proper amount of lime, agitate and draw off to the settlers. We soon found, however, that the thorough agitation was not only not necessary but in fact detrimental to a perfect settling, as the precipitate lost its flocculent character and did not leave a perfectly clear solution. It was further difficult to maintain the flow into the settlers at a constant rate—a condition, which is very essential when working continuous settlers. After some experimenting with baffle plates arranged horizontally above each other, which did not prove satisfactory on account of the enormous amount of foam created, we finally decided that the simple scheme of running the water and the lime together

in a continuous stream into the same tank gave the best results. This tank has an overflow to the settlers about three feet from the bottom and is provided with an agitator which moves very slowly.

The regulation of the lime supply offers no difficulties. The man in attendance tests the treated water for alkalinity at fixed intervals. There is a certain relation between the alkalinity and the amount of lime added, and any variation in the amount of lime is indicated by a corresponding variation of the alkalinity. When using the normal quantity of lime the titer of the water is about one-fourth of the alkalinity of a completely saturated lime solution.

The lime is slaked with hot water in a trough-like iron tank. In the tank revolves a horizontal reel made of coarse 1/4-inch netting. The lime is charged into this reel through a funnel-shaped opening on the side of the tank. The lime milk is pumped to a diluting tank, in which it is made up to the desired gravity. From there it runs over a fine screen into a storage tank provided with an agitator. A centrifugal pump is connected to this tank. The lime milk is kept circulating through a pipe line, which runs up to the mixing tank and back to the storage tank, and the supply pipe to the mixing tank branches off from this line. In this way a constant supply of lime milk of uniform strength is insured.

The settlers are built like gluten settlers, with conical bottom. The diameter is 14 feet; the cylindrical part is 22 feet high. The capacity is about 28,000 gals. The treated water distributes itself into troughs running over the settlers. Each settler has in the center a vertical pipe, 15 inches square, connected with the bottom of the trough. This pipe ends about three feet from the bottom of the cone.

The supply to each settler is regulated by raising or lowering plugs, which fit holes in the bottom of the troughs over the vertical pipes. The water runs downward through the vertical pipe, rises slowly on the outside and overflows into troughs, which lead to a sewer discharging some distance out in the lake. The precipitate stays in the lower part of the settler and the sludge is drawn off continuously through the pipe at the bottom of the cone. There are 21 settlers, of which 16 are used for the first settling. The sludge from these settlers is pumped to the five so-called second settlers. From here it is pumped a considerable distance to the old Dry Starch House at the southern end of the plant. The sludge is filter-pressed here, the presscake is broken up, loaded upon trays and dried in kilns in the same manner as starch.

What to do with this presscake has been and is still a problem. Owing to the excess of lime, the only use which could be made of this product would be as fertilizer. As both the protein and the phosphoric acid are low it could command only a very modest price. Whether this would be profitable depends upon the proximity of a market. Part of the presscake is used for neutralizing the concentrated steep water, which contains a certain amount of acid phosphate and of organic acids. It is well adapted for this use, and by distributing the same among the other plants consid-

erable quantities of this product have been disposed of. The bulk of the presscake, however, is bagged and stored away until some use is found for it.

These notes on the treatment of starch waste have, I hope, given an idea of the nature of the problem and of the manner in which the company has tried to solve the same in this particular case. Sanitary standards and requirements become higher gradually and the chemical industry in particular is confronted more and more with the necessity of having to consider its various problems of waste, not only from the point of view of recovery and utilization but also in regard to their disposal to the satisfaction of the sanitary interests, which may call for strict and rigorous requirements without themselves being always able to offer any guide or suggestion as to the solution of the problems.

CORN PRODUCTS CO., CHICAGO.

PLANT AND MACHINERY.

SAMPLING AND PREPARATION OF RAW MATERIALS FOR ANALYSIS AT SOUTH WORKS, ILLINOIS STEEL CO.

By WALTER B. WILEY.

Chemical control in the manufacture of steel has at present not reached its ultimate importance, but, during the past decade, rapid steps have been made in that direction.

More and more is constantly demanded in this line, and at the South Works of the Illinois Steel Co. earnest and careful efforts are made to meet these requirements.

Here, the taking and preparation of large and representative samples of all raw materials, entering into the making of steel, is a matter of routine controlled by strict supervision and by intelligent methods, the result of many years of experience and much experiment.

There are two distinct theories as to the proper method for reduction of samples to laboratory requirements, crushing and grinding, and each has its advocates.

The champions of crushing, by means of rolls, insist that by this method there is less danger of contaminating the sample by the introduction of small particles of iron which may also carry with them phosphorus and other elements, thereby vitiating the value of chemical analysis.

On the other hand, grinding is probably much more rapid and the machinery required more compact.

The grinding method was chosen at South Works, but the chance of contamination of samples avoided, or at least greatly minimized, by the use of manganese steel for all grinding surfaces.

Sampling of raw materials must always be an integral part of modern steel-making, therefore its housing should be in permanent structures. The sampling house, preferably of concrete or brick construction, should have few exposed beams or ledges to furnish lodgment for the dust and dirt consequent to crushing, thereby making cleanliness possible and

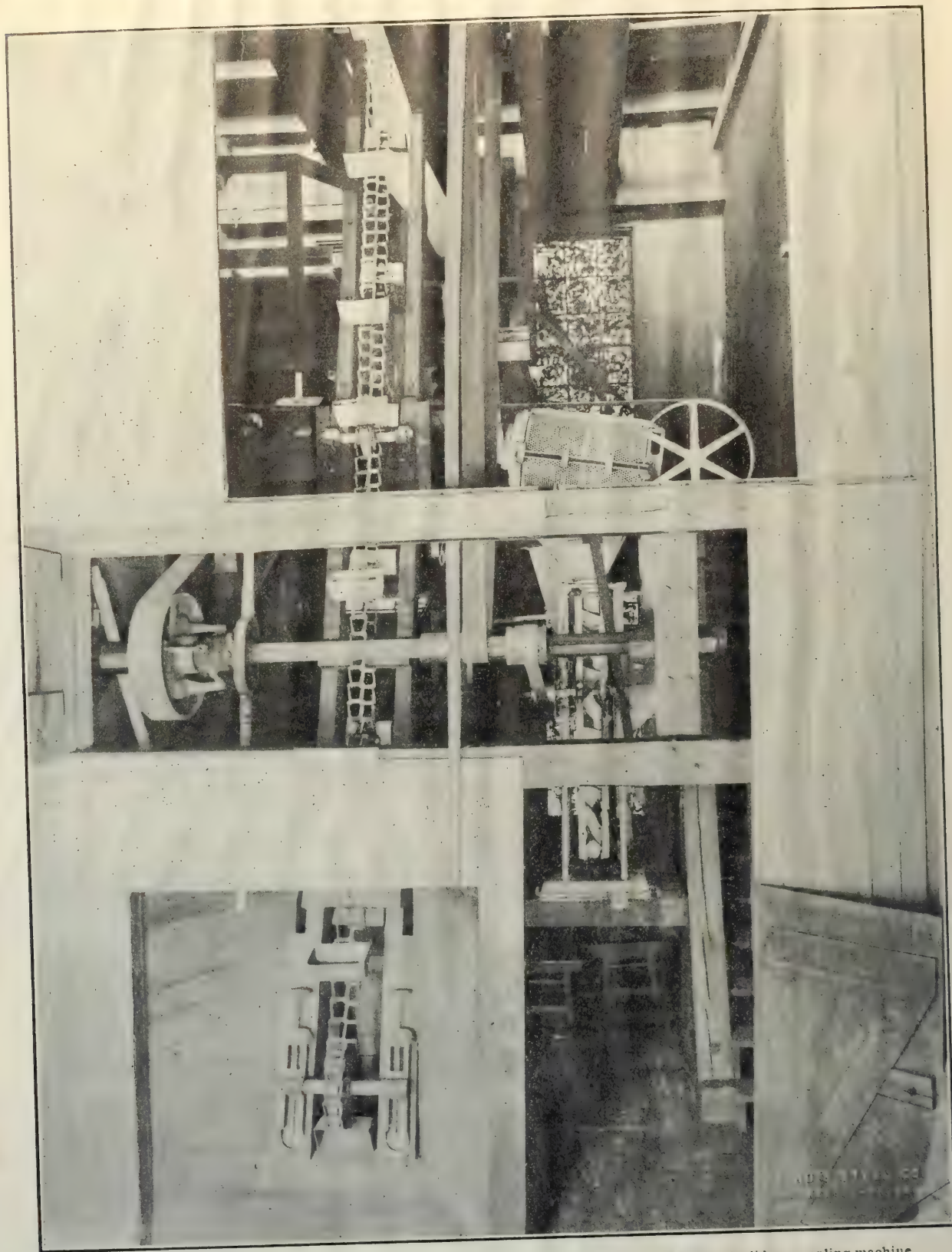


Fig. 1.—Machinery for primary ore crushing, 30 size. Gates crusher; revolving screen and Foster-Coolidge sampling machine (enclosing wall partially removed).

easy to maintain. Provision for an abundance of light and ventilation is an absolute necessity.

In 1907, when the present South Works sampling house was built, certain local conditions made necessary a frame construction, covered outside with corrugated iron and ceiled inside. At that time it embodied, probably, the best and most advanced ideas for the rapid and accurate mechanical preparation of large samples. Since then a few minor changes have been made to improve details and keep abreast with the times, so that at present the equipment is modern, in the best sense.

In the still room is a Jewell still which furnishes all the distilled water used by the plant, for laboratory and other purposes. Here are kept shipping notices of all raw materials and by which our sampling is checked.

The rubbing room is provided with two open-hearth steel, properly tempered, bucking boards 24" by 24" with 45 pound mullers for the same, used for reducing samples to laboratory fineness. There is also an Iler disc pulverizer, speeded to 600 r. p. m., which aids in the final preparation of certain samples. Chilled steel mortars are used to finish samples like coke and

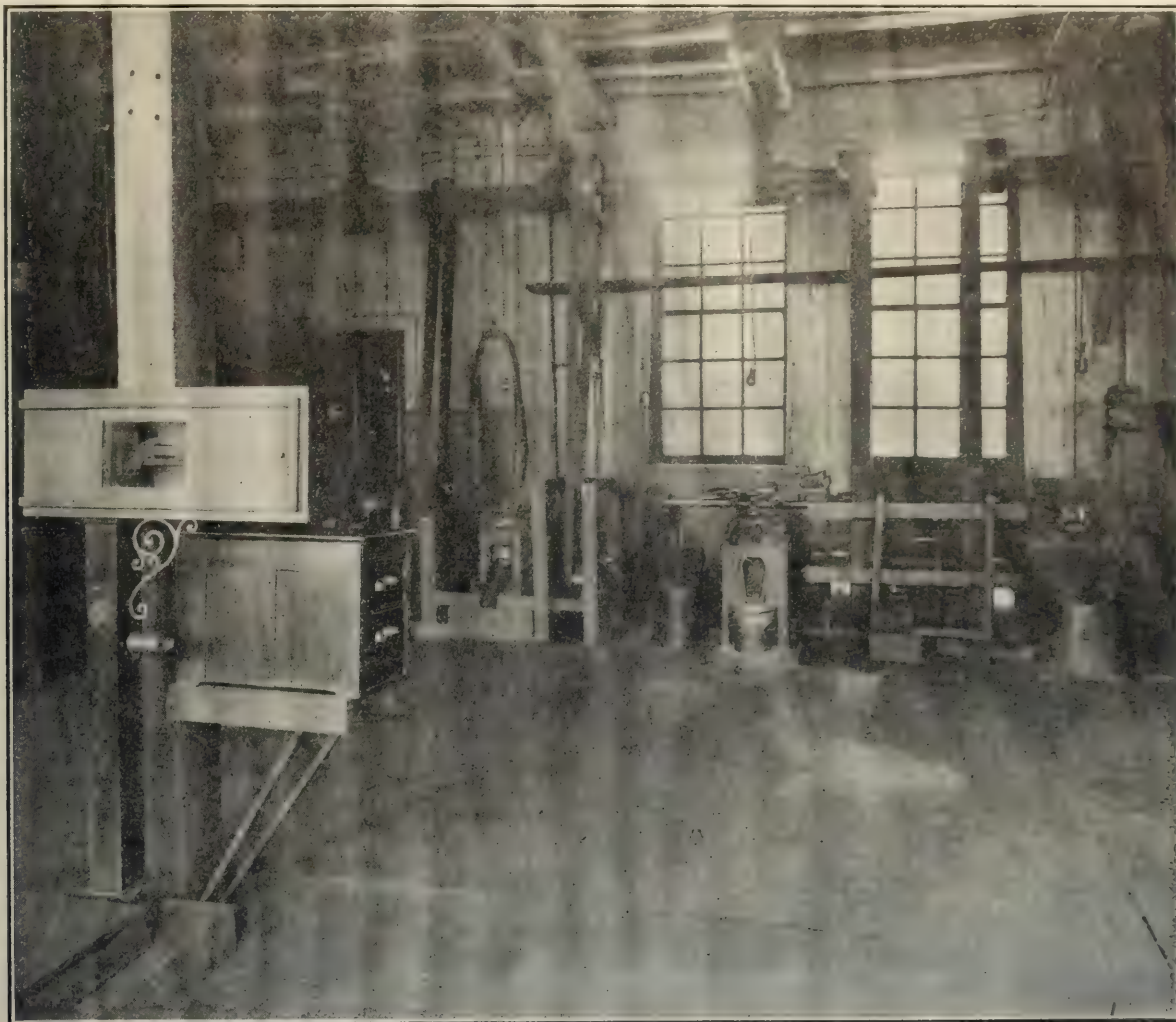


Fig. 2.—Machinery for intermediate grinding.

The house consists of a main structure 53' by 38' with a wing 30' by 22'.

The wing, provided with dust-tight bins and boxes, to avoid contamination, is used for storing cumulative samples which are worked up at weekly, semi-monthly and monthly intervals. Here, also, is installed the 10 h. p. constant speed induction motor which furnishes the power necessary for operation of all the machinery.

The main building is divided into a crushing room 40' by 38', a rubbing or finishing room 9' by 13', a still room 13' by 20' and an office 9' by 13'.

scales for which, to date, no machine has been found capable, by us, of preparing properly.

The crushing room is provided with a floor of smooth steel plates, to facilitate the mixing and quartering of samples. Six drying pans, 6' by 6.5' with double bottoms and heated by steam, are located here and used for drying ore samples before crushing. A group of machinery consisting of a "O" size, style "D" Gates gyratory crusher, a revolving screen with 1/2" circular perforations, a Foster-Coolidge automatic sampling machine and all necessary shafting, conveyors and hoppers is installed in a space 17'

by 19' in one corner of the crushing room, head room for the machinery being provided by a tower. This group is used solely for the primary crushing and reduction of ore samples and is enclosed to keep the consequent dust from the balance of the house.

In this room are also located one Blake jaw crusher; one Style "F" Gates gyratory breaker; two Gates sample grinders, one style "B," the other style "A;" and a steam-heated oven for determination of moisture in materials.

A scale, built to our specification by the Buffalo Scale Co., which frequent tests show to be sensitive to 1/100 of a pound with a load of 300 pounds, is placed perfectly level on a concrete pier and is

they are received. By this means the portions or increments making up the sample are scattered throughout the mass and more nearly represent the material. This method assures an impartial and representative sample of cars which have been improperly loaded by the shipper or the surface improved by the material settling during transit. It is very seldom that surface samples are taken and then only when it is desired to quickly get a line on a material and these cars are resampled on unloading.

Ore is sampled by the methods described in a former issue of THIS JOURNAL (1, 107 to 115), but the preparation varies slightly from the method there described.

Material, such as coal, refractories, etc., received

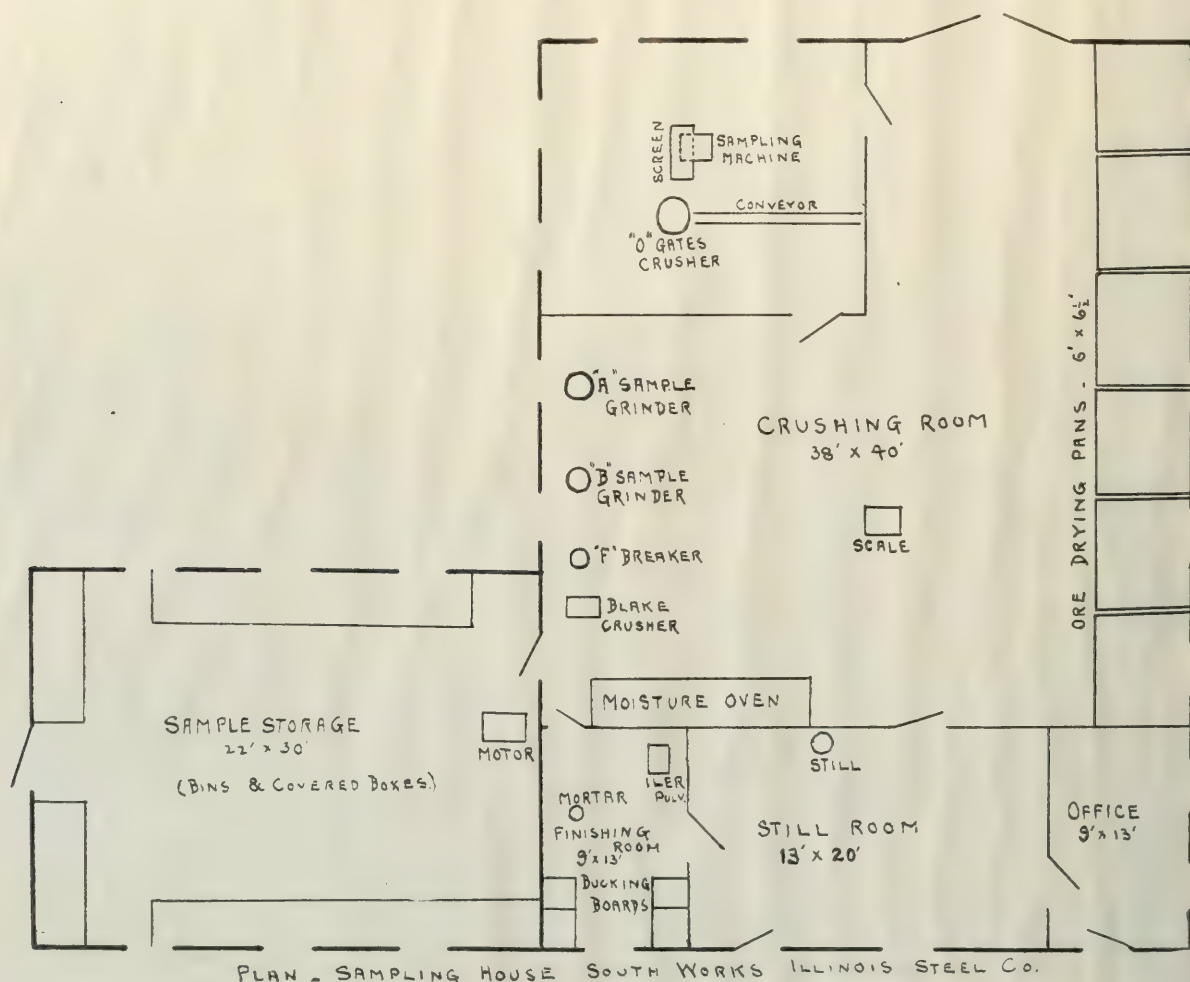


Fig. 3.

used for weighing moisture and fineness samples. It is provided with three beams graduated to 5 pounds, 1/10 pound and 1/100 pound, respectively.

An electric air compressor with suitable tanks, piping and hose is provided for cleaning machinery, sieves, etc.

Each machine is fitted with tight and loose pulleys which permits the operation of any or all, as required.

Guard rails, belt shields and gear covers are placed at each point needed to insure absolute safety.

Sampling.—All samples of materials are taken during the unloading of either boats or cars in which

in cars and unloaded by shoveling, is sampled on the exposed faces, after the bottom of the car is reached, by taking equal portions from points touched at measured intervals.

Coke is generally received in side dump cars which quickly and completely empty themselves, so the only possible chance to obtain unloading samples is by holding a pail in the descending stream, thereby getting both fines and coarse in the samples. This method may be subject to some criticism, but more trustworthy results have been obtained than by any other we have employed to date.

Preparation of Samples.—Ore samples, whose average moisture content is about 10 per cent., are placed in the drying pans and dried sufficiently to prevent sticking in the machinery. They are then removed and placed in front of the conveyor, to which they are fed by means of a shovel, and elevated to the hopper above the crusher. This hopper is provided with a screen with 1/2-inch perforations, the fines are conveyed by a chute to the discharge spout of the crusher, the lumps over 1/2 inch size being ground by the crusher, and, joining the fines, all delivered to a revolving screen with 1/2-inch perforations. There is usually a small percentage of oversize which escapes through openings at the lower end of the screen, and is returned to the crusher for further reduction.

The half-inch material from the screen is delivered to a hopper above a Foster-Coolidge automatic sampling machine, which accurately reduces the original sample to 1/16, which is retained in a covered sheet iron box, rejecting 15/16, which is delivered to wheelbarrows outside the building, put in bins and afterward returned to the blast-furnace stock piles.

This sampling machine consists of a series of four hoppers and four split shovels which travel in opposite directions and horizontally, thus cutting very rapidly the vertically descending stream of ore. Before the installation of this machine all mixing and quartering was done by hand at considerable expense of time and money, and a long series of experiments has shown that the results from the sampling machine are obtained quickly, accurately and cheaply. Usually about 50 or 75 pounds of ore remain in the boot of the oversize conveyor; this is removed, ground in the "F" style Gates breaker, and put through the sampling machine to add its proportion to the sample. The 1/16 of the original sample is now ground by the style "B" Gates sample grinder, which grinds and automatically halves it, the discard going to one side of the machine and the sample to the other. By repeating this several times and gradually tightening the machine the sample is reduced to about 5 pounds that will all pass a 40-mesh sieve. This is intimately mixed, quartered and finished by means of the Iler disc pulverizer, having manganese steel discs, and bucking-board to pass a 100-mesh sieve. It is again mixed thoroughly, spread out very thin, and small portions selected from all parts of the sample and placed in a 6-oz. glass-stoppered bottle for the laboratory sample.

The cones and concaves of the sample grinder are made of manganese steel from patterns of our own design, and one set used for ore exclusively.

All machines are thoroughly cleaned by means of compressed air and brushes after working each sample.

For the past two years the experiment has been tried of giving the ore samplers and other employees, engaged in the preparation of these samples, free access to the results of ore analysis, both of our own samples and of those of the producing mines. It has proved of considerable benefit by giving the men

a greater interest in their work, and, doubtless, an extension of the plan would be profitable.

Coal.—Samples are worked weekly, being crushed to 1/2-inch size with the Blake jaw crusher, thoroughly mixed by the cone and ring method, and reduced to about 60 or 70 pounds by Cornish quartering. The sample remaining is further ground and reduced by the style "A" Gates sample grinder to about 5 pounds, all passing 40 mesh, finished with the Iler pulverizer and bucking-board to pass 80 mesh and the sample taken out for analysis.

Coke.—Samples are worked daily and semi-monthly, the preparation being the same as for coal except that the final reduction to 80 mesh is done by pounding in a steel mortar, as, owing to the nature of coke, it is impossible to rub it fine.

Refractories and other material are prepared at the end of the month and if crushing to 1/2-inch size is necessary the Blake crusher is used, the medium grinding done with the "B" Gates and the finishing according to their character, made with the Iler pulverizer and bucking-board or by pounding in a mortar.

Moistures.—Moisture is determined in each cargo of ore unloaded, by taking an accurately weighed 100-pound sample out of the ore sample and drying for 12 to 18 hours, as found necessary by experience, in a steam-heated oven regulated to 100° C. The dried ore is carefully weighed and returned to the main sample. As the scale is accurate to 1/100 of a pound the loss of weight represents percentage direct, to the second decimal place, without further calculation.

Moisture in coal, coke, and other material is determined as above but on 25 pounds of the 112-inch crushed material, the loss multiplied by 4 gives percentage direct.

Fineness.—Each ore received, flue dust and flue dust sinter are shaken through a series of 18-inch sieves and the percentages remaining on 2-, 8-, 20-, 40-, 60-, 80- and 100-mesh sieves and through a 100-mesh reported monthly by the sampling house. Cumulative samples representing by tonnage the ore and other material are saved, dried, mixed thoroughly and reduced by quartering to 100 pounds and put through the sieves, the portions of different fineness accurately weighed, the weights representing percentage without further calculation. Frequently very small samples of material are received for fineness determination and a set of small brass sieves and a Troemner balance are provided and used for this purpose.

CONCLUSION.

The sampling house is only operated on day turn, and, to date, its capacity for turning out finished samples has not been reached. Probably the amount of work could be more than doubled by running longer hours, but so far this has not been found necessary.

During the ore season of 1910, just completed, 3,825,963 gross tons of ore were unloaded and sampled at the two docks of South Works. From this ore, received in 522 boats, 863 samples (wt. 879,026 lbs.) were taken and prepared.

The complete data for the year 1910, just available, an average year, shows the following miscellaneous materials were sampled:

Cars.	Material.	Weight of samples.	
		Samples.	Pounds.
30,265	Coke.....	3659	302,657
10,988	Coal.....	917	109,885
4,052	Limestone.....	2107	49,072
794	Refractories.....	378	19,840
105	Ferro-alloys.....	105	1,285
109	Fire-brick.....	113	2,739
696	Scale and cinder.....	264	26,190
58	Slags—various.....	3201	5,210
1,235	Miscellaneous.....	322	27,477
48,302		11,066	544,355

LABORATORY, SOUTH WORKS,
ILLINOIS STEEL CO.,
December 31, 1910.

NOTES AND CORRESPONDENCE.

EFFICIENCY IN ACID PHOSPHATE MANUFACTURE.

In even so simple a process as the manufacture of acid phosphate a high efficiency is not always attained. At the close of the spring season of 1908, at this plant, the average insoluble phosphoric acid on the acid phosphate produced was 2.50 per cent. and on the phosphate shipped was 1.74 per cent. About that time the writer was given charge of the acid phosphate manufacture, and since that time the same equipment has been producing acid phosphate with an insoluble of 0.75 to 1.00 per cent. and shipping this product out with about 0.30 per cent. insoluble. This one change means an increase in efficiency of nearly \$20,000.00 annually.

A careful attention to details has brought about this result, but just what part of the change is due to each no one can tell. During the period mentioned, the change has been made from Tennessee to Florida rock, but the changes referred to and some of the results obtained were on Tennessee rock so that this change does not materially affect the points in this paper.

The more important details and the attention given them are as follows:

Proportion of Acid and Rock.—The amount of acid required for the most efficient manufacture of acid phosphate can be determined only by trial for each kind and grade of rock. That quantity of acid which will give an insoluble phosphoric acid of 0.75 to 1.00 per cent. at 48 to 72 hours old has proven best under our conditions.

Strength of Acid.—Acid is used which when calculated to 60° F. will show 52° Bé. Whether a formula calling for 51, 52 or 53 acid is used does not seem to be so vital as the necessity of having a constant strength of acid to use after the formula has been decided upon. We do not allow the strength to vary more than 0.3° Bé. either way from 52° when calculated to 60°.

Temperature of Acid.—In using the den system for acid phosphate manufacture the temperature of the acid does not seriously affect results, but in the single car open dump system the temperature must be above 100° F. and should be 130° for good work. If this is not the case the reaction does not start in the

mixer promptly and a wet sloppy mixture is dumped on the pile which splatters so that it never properly reacts. For efficient work with the open dump system the phosphate when dumped from the car must "set up," that is, must remain where it is dropped, not being liquid enough to run. The temperature of the acid is the most important factor in attaining this end.

Grade of Rock.—Different kinds of rock and even different grades of the same rock require different quantities of acid. It is therefore evident that economy demands keeping the different kinds and grades separate or, if this is not possible, using a definite and constant mixture. Unless excess acid phosphate storage room is available a loss will be experienced in the open dump system through the mixing of various grades of phosphate. Plant operation can be made more efficient therefore if one grade and kind of rock only is used.

Fineness of Rock.—The results above cited have been obtained with rock ground until 95 to 97 per cent. pass a 60-mesh screen. 87 per cent. through the same screen will not give as good results and it seems doubtful if finer grinding would be more economical although some plants are operating on a finer rock dust.

Time in the Mixer.—The remarks above on condition of the acid phosphate when dumped on the pile are to the point here. The charge of acid and rock must be held in the mixer until it has reached a state that will give the required thick, pasty mass on the pile. The time required to do this will vary with the kind and fineness of the rock, the strength, quantity, and temperature of the acid but with these all properly regulated the time will be between 1 and 3 minutes.

Time in the Pile.—As far as the operating conditions of the plant will allow, the acid phosphate should be allowed to lie in the pile and cure as long as possible, the limit being when the interest charges on the money invested exceed the increase in value due to lower insoluble and better mechanical condition. The reduction in insoluble is, of course, slow after three months have passed.

When it is known that the acid phosphate must be used up in a few days or weeks after it is made, it is possible to use enough acid to reduce the insoluble to 0.40 per cent. by that time, but this may not be advisable because of the accompanying sacrifice of the mechanical condition. The proper course to pursue is a matter that must be left to the judgment of the man in charge.

In conclusion, the key-note to efficiency in acid phosphate manufacture by the open dump system is an untiring watchfulness and attention to details.

With the den system slightly less of this is demanded but the additional expense of one handling of the acid phosphate is required.

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LABORATORY DISTILLATIONS OF WATER GAS TAR.

The information regarding the composition and properties of water gas tar available in books and

journals is scanty and not altogether reliable as applied to the modern American product. A large proportion of this tar is burned as fuel although some is used for road dressings and an unknown amount is distilled. If, as would seem probable from its resemblance to coal tar, the distillation of this tar will yield valuable products, a fuller knowledge of its composition than is to be found in the literature is desirable.

This paper gives the results of the fractional distillations of samples of water gas tar obtained at different points in the purifying system where gas was being manufactured by the Lowe system for making carburetted water gas. The gas oil is cracked in a stream of carbon monoxide and hydrogen, and at the plant where the samples were collected at a temperature of from 1400°–1420° F. By this procedure a large percentage—in the neighborhood of 25 per cent.—of the oil used is converted into substances which do not remain permanently in the gas but appear as tar removed by the purifying system. The petroleum oil used for carburetting is obtained from different fields, and varies somewhat in the nature of the constituent hydrocarbons. An Oklahoma oil was in use at the time the samples under analysis were obtained.

The gas after it leaves the superheater of the water gas set passes through a water seal and up the board scrubber which cools the gas to a considerable extent and removes about 60 per cent. of the tar. The tar taken out by the seal pot and the board scrubber is called the "separator tar." From the board scrubber the gas passes to the water-cooled condensers where the "condenser tar" is removed. Between the condensers and the Pelouze and Audouin tar extractor is placed the exhaustor, and at this point the gas shows a temperature varying but little from 140° F. The "P and A" tar is taken out by the Pelouze and Audouin extractor. The gas passes next through air-cooled condensers followed by a shavings scrubber; the tar separated in these two pieces of apparatus is known as the "shaving scrubber tar." A small amount of tar is deposited in the connecting pipes between different parts of the purifying system, and in general drains forward. It will be noted that the different samples of tar are removed at progressively lower temperatures as the gas passes from the set to the last step of purification, and by the time it leaves the shaving scrubber it is down to about 105° F. and practically free from tar or fog.

In marked contrast to coal tar, water gas tar contains but little free carbon or soot. The samples worked with contained only traces of material insoluble in carbon bisulphide. The amount of nitrogen is small, an analysis showing but 0.08 per cent.

As might be expected, the specific gravities of the different tar samples were progressively less from separator to shaving scrubber. The following values were found: separator tar, 1.090; condenser tar, 1.081; P & A tar, 1.068; and shaving scrubber tar, 1.056—all at 15.5° C.

In carrying out the fractional distillations of the samples, advantage was taken of the better separation obtainable by the aid of a Hempel column and of the almost perfect temperature control afforded by electrical heating by means of a resistance coil immersed in the boiling tar as suggested by Richards and Matthews.¹ To effect this a special form of flask was devised as shown in the figure. By means of the tubulature, a pair of electrodes is introduced, and between them at the bottom of the flask is a resistance coil. During the distillations the flask is placed inside a glass jar, so that all drafts are avoided and radiation diminished, and yet the contents are in plain view. With this arrangement the current from a 110-volt lighting circuit controlled by a rheostat and an ammeter gives well-nigh perfect heating. The constriction in the neck of the flask provides

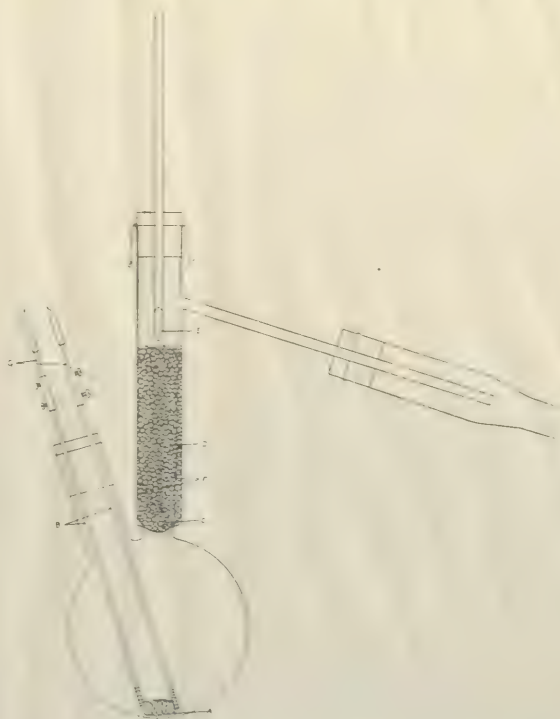


Fig. 1.—Apparatus for laboratory tar distillations.

(A) resistance coil; (B) electrodes; (C) gauze supporting beads; (D) glass beads of Hempel column; (E) Thermometer bulb; (F) wires holding the supporting gauze; (G) wires connecting through ammeter and rheostat to lighting circuit.

support for a wire gauze upon which rest the glass beads of the Hempel column. It is a convenience to attach slender wires to this supporting gauze so that it and the beads may be lifted in and out without tipping the flask, the slender wires between the cork and the neck of the flask causing no inconvenience.

It was necessary in running the distillations to pause at 200° C. for a change from the water-cooled condenser to an air condenser, and to substitute a high range thermometer for the lower range instrument required for the early stage of the distillation.

A large number of fractions were taken in each distillation and the results are expressed as curves

¹ J. Am. Chem. Soc., 30, 1282; 31, 1200.

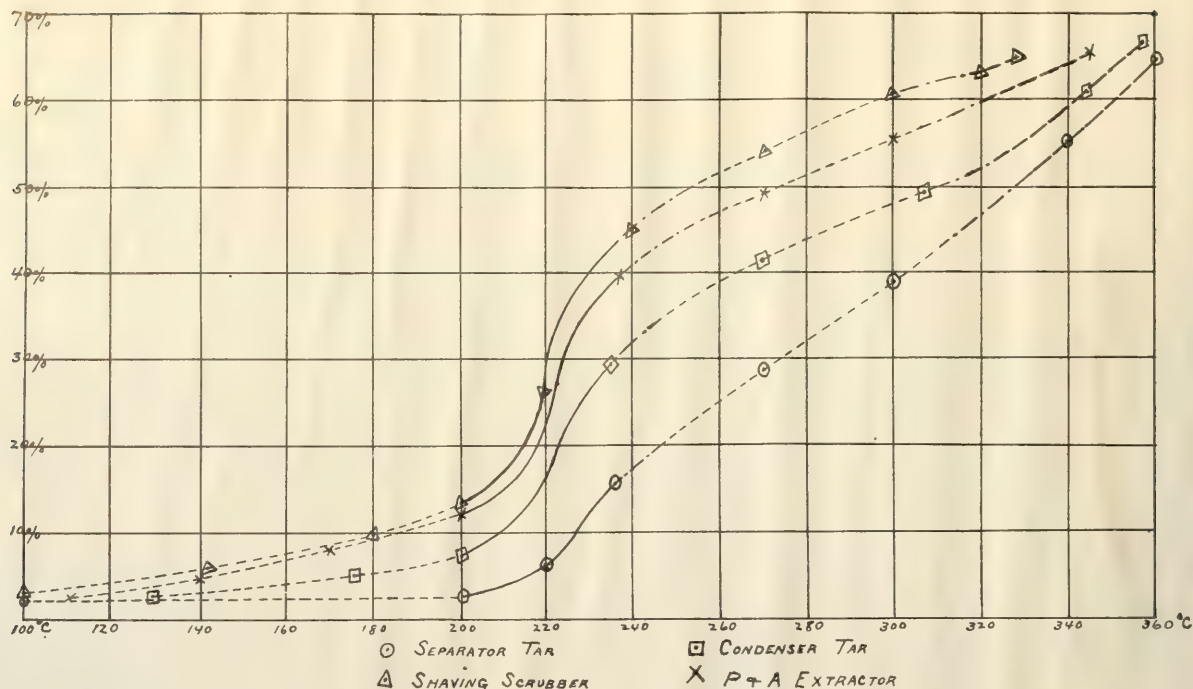


Fig. 2.

in which solid lines indicate distillates solidifying on cooling, dotted lines those remaining liquid, and broken lines the intermediate consistencies. As foreshadowed by the differences in specific gravity, the tars vary in the proportions of high- and low-boiling constituents, and become progressively lower-boiling from the separator tar to the shaving scrubber tar.

The fractions were particularly satisfactory in color and general character. The low-boiling liquid distillates were pale yellow, clear liquids, the naphthalene fractions almost pure white and solid at room temperatures, and the high-boiling portions of decidedly better color than the corresponding fractions from coal tar. There is a similarity in the general appearance of the distillates from coal tar and water gas tar, especially in the portions boiling below 300 °C. The high-boiling portions of the water gas tar are noticeably less solid than those from coal tar. In the case of the latter the distillate becomes decidedly hard as the temperature rises. Solid distillates are also obtained from the water gas tar above 300 °C., but there is a range between 340° and 360° where with a good fractionating device a clear, heavy liquid distillate is obtained, which after standing shows some crystals but does not become solid, a marked contrast to the distillate from coal tar at this point.

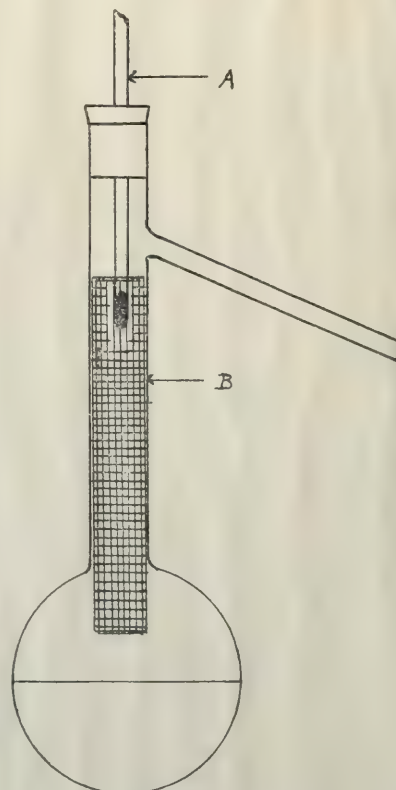
The differences between the distillates from the different samples of water gas tar which had separated at different points in the purifying system were apparently quantitative rather than qualitative, the distillates coming off from the different ones at the same temperatures being indistinguishable.

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NOTE ON THE DISTILLATION OF TARS CONTAINING WATER.

Great difficulty is met with at times when it is necessary to distil a mixture of tar and water. Some gas tars contain as high as 75 per cent. of water in the form of an emulsion that will not break on long



A = Thermometer.
B = Wire gauze.

standing. If this emulsion is distilled from a retort or ordinary distilling bulb it is almost sure to "bump over," the water condensing on the thermometer or sides of the neck and dropping back into the heated tar, causing it to bump. This is prevented by making two concentric cylinders of "30 mesh" brass gauze, which are slipped into the neck. This prevents any tar that does bump from going over at the beginning of the distillation. After the distillation has begun, the brass cylinders conduct heat upwards and any water collecting above is volatilized from the gauze instead of dropping back into the tar. There is plenty of room for the thermometer bulb inside the inner cylinder. Besides preventing bumping, the gauze cylinders act to some extent as a Hempel column and give a better service than the bare distilling bulb. The gauze is suspended by small wires that are held in place by the cork. C. R. DOWNS.

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PRECIPITATION OF SULPHUR FROM DILUTE LIME-SULPHUR SOLUTIONS.

A recent development in the use of the lime-sulphur solution for spraying purposes is as a summer fungicide, for which purpose it promises to supplant to a considerable extent the older Bordeaux mixture. The dilution is necessarily much greater than that used in the winter, since injury to the foliage would otherwise result, but as yet there is no unanimity of opinion among authorities as to the relative degree of this dilution, and sufficient data from practical results has not yet accumulated to permit of any positive conclusions.

The range of dilutions recommended in several publications is shown in Table 1. For the sake of comparison, the original data has been recalculated to the basis of a density of 1.30, assuming that the density of a solution varies inversely with the number of dilutions. This is not strictly true in the case of lime-sulphur solutions, but is accurate enough for the present purpose.

TABLE 1.

Authority.	Solution used for:	Gals. water added	
		Aver. sp. gr. considered.	to 1 gal. L.-S. sol. sp. gr. 1.30
Niagara Sprayer Co.	General summer fungicide	1.28	42
The Rex Co.	Apple, pear, quince	1.28	31-42
	Peach, plum, cherry, grape	1.28	53-79
N. Y. (Geneva) Agricultural Expt. Station	Apple	1.294	36
Penn. Agr. Exp. Sta.	Apple and pear (scab)	1.30	19-29
	Foliage tests	1.30	14-59
	Scab and brown rot, stone fruits	1.30	37-59
	Scab and brown rot, experimental	1.30	99
Va. Agr. Exp. Sta.	Apple, pear	1.294	33
	Peach, plum, cherry	1.294	130

The minimum and maximum dilutions recommended are respectively 14 and 130 gallons of water to 1 gallon of 1.30 lime-sulphur solution. Practical results already secured would seem to indicate that in the case of apples a dilution of 30 gives a weak enough solution, but for more tender fruits a greater dilution will probably be necessary. There is, however, a factor entirely independent of spraying results which

will be found to limit the dilution safely attainable, the precipitation of free sulphur by too great an excess of water.

While investigating the properties of concentrated lime-sulphur solutions, the writer noticed that a precipitate of sulphur quickly formed after running water into a beaker from which such a solution had just been poured. It appearing not improbable that this behavior might prove an important consideration in the dilution of solutions for spraying purposes, further attention was at once given it. The view is now quite generally held that the calcium-sulphur compounds, giving to the solution its principal value as an insecticide and fungicide, are the two higher sulphides CaS_4 and CaS_6 . If by excessive dilution, these are broken up into free sulphur and various compounds, a direct loss of efficiency occurs, destroying, in a great measure, the value of the solution except insofar as a mixture of sulphur and water would be of benefit.

Qualitative tests showed that the precipitation took place slowly if comparatively small amounts of water were used for the dilution, but almost immediately if large volumes were introduced. The relative amount of sulphur deposited became greater as the dilution was increased, while the color of the precipitated sulphur ranged from orange to milk-white under the same conditions. There seemed to be no difference in results whether the solution was added to water or *vice versa*.

A short series of quantitative tests was then planned, in order to secure data for use in practical work. A solution was taken for dilution having a density of 1.03977, it having been already diluted up from a concentrated solution. Six 5-cc. portions were pipetted into beakers containing appropriate volumes of water, the time of addition was noted, and the beakers were allowed to stand until sulphur was precipitated. The results are shown in Table 2.

TABLE 2.

No.	Cc. water added.	Added at:	Dil. from sol. taken.	Dil. from sp. gr. 1.30.	Time ppt'd.	Hours.
1	15	7.56 A.M.	4	30.18	—	—
2	25	7.57 A.M.	6	45.26	—	—
3	35	7.58 A.M.	8	60.35	—	—
4	50	7.59 A.M.	11	82.98	1.30 P.M.	5 ¹ / ₂
5	80	9.14 A.M.	17	128.25	11.30 A.M.	2 ¹ / ₂
6	150	9.24 A.M.	37	233.90	9.35 A.M.	11 ¹ / ₂

Upon prolonged standing even the first three developed traces of a precipitate, but this was probably due to atmospheric action and would have been prevented had the solutions been protected by a layer of oil. As was the case with the qualitative tests, the more dilute the solution the greater the relative precipitation of sulphur and the more quickly it was thrown down.

In order to ascertain whether this precipitated sulphur could be redissolved a trial was made with precipitation No. 5, boiling the solution and sulphur together for some time. Apparently about half of the sulphur dissolved, but long before the solution was cool it was reprecipitated. A second boiling failed to give a similar effect, the sulphur having apparently settled in an insoluble form upon cooling.

This shows that when a precipitate is once formed in a solution, the latter is spoiled for spraying purposes.

From the results in Table 2 it appears that a lime-sulphur solution of sp. gr. 1.30 may safely be diluted with 60 times its own volume of water without precipitating free sulphur, but that larger volumes will cause precipitation, the length of time before the beginning of which ranges from a few minutes to several hours. It seems probable that different solutions will give variations from the figures given here, as lime-sulphur has a great tendency to vary in behavior under parallel conditions, but the general results will be found in accord. As applied to actual work, the conclusion is that if a solution will be entirely sprayed out within two hours, after dilution it is safe to add as much as 125 gallons of water to 1 gallon of 1.30 solution, but if it may have to stand for several hours not over 60 to 70 gallons may be added without precipitating out free sulphur and spoiling the solution.

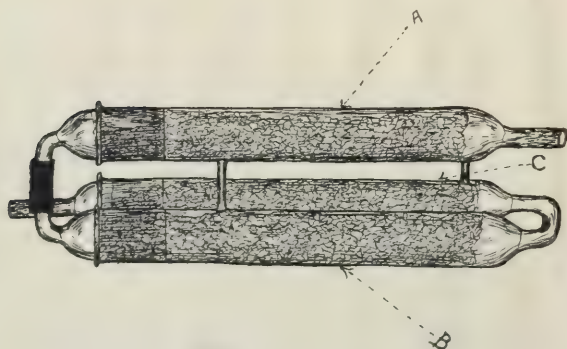
L. T. BOWSER.

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A NEW ABSORPTION APPARATUS.

This apparatus was designed primarily as weighing tubes replacing the U-tube in the determination of carbon dioxide by the soda-lime method. It may also be used to advantage in replacing the U-tube where the latter contains a solid absorbent used as a trap for gases.

The apparatus consists of three glass tubes 15 mm. in diameter and 100 mm. long. The tubes are lettered A, B, C, in the drawing. The right end of tube A



is drawn out into a tube of 5 mm. in diameter and 15 mm. long. The left end of tube A is fitted with an open, hollow, ground glass stopper drawn out into a tube of 5 mm. diameter and bent at a right angle. The left end of tube B is fitted with a similar stopper and the two stoppers are connected by a piece of rubber tubing. The right end of tube B is drawn out into a tube of 5 mm. in diameter and with a U-bend is fused onto the drawn-out end of tube C. The left end of tube C is fitted with an open, hollow, ground glass, stopper drawn out into a tube 5 mm. in diameter and 15 mm. long. The tubes are attached to each

other by short pieces of glass rods fused onto their sides.

To charge the apparatus, the stoppers are removed and a small plug of glass wool or cotton is placed in the opposite ends of the tubes. Tubes A, B, and two-thirds of tube C are filled with soda lime. The remainder of C is filled with anhydrous calcium chloride. The gas enters at the right end of tube A and circulates towards the left end of C until absorbed.

The calcium chloride and the soda lime should be crushed to pass a six-mesh sieve and caught on a twenty-mesh. The apparatus charged with lumps of this size weighs about 75 grams and will afford about eight determinations of CO_2 , using $\frac{1}{4}$ gr. of a carbonate containing 40 per cent. CO_2 , before recharging.

The advantages of this apparatus over the U-tube used for a similar purpose are:

1. This apparatus affords one-third more absorbing space than a U-tube of the same dimensions, thus affording a greater number of determinations before recharging.

2. The apparatus can be laid on the balance pan, whereas the U-tube must be suspended to the beam.

3. The apparatus will accommodate a larger amount and a greater variety of absorbing materials when used as a trap for gases than the U-tube.

The apparatus was made by Messrs. Eimer & Amend; cost \$2.50, f. o. b. New York.

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TENSILE STRENGTH OF HAIR CLOTH.

Following the recent edict of the Chinese emperor abolishing the wearing of queues, the European markets have been overstocked with human hair. The price of this article has fallen almost one-half, while the import has been doubled.

The usual use of human hair has been in making wigs, switches, etc. The increased production demanded an outlet for the surplus. According to a recent report made by U. S. Consul Ingram, Bradford, England, British weavers are furnishing the outlet by utilizing the material in weaving. Hair is used both alone and in combination with other fibers. Ingram says: "The hair (10 to 12 in. long) is first disinfected, then spun into yarn and woven into cloth. The finished fabric comes in 20-inch or 30-inch widths and up to 90-yard lengths. No dye is used, the color being the natural tint of the hair. The fabric is intended for interlining for men's wear and possesses the advantages of being absolutely *unbreakable, unshrinkable and uncreasable.*"

Several samples of these fabrics, the product of an enterprising Bradford weaver, have been examined for strength:

- To. 1a. Weight per square yard, 8 oz.
Warp, wool, 40 lbs. tensile, per inch.
Filler, goats' hair, 28 lbs. tensile, per inch.
- To. 1b. Weight per square yard, 9 oz.
Warp, wool, 57 lbs. tensile, per inch.
Filler, goats' hair, 42 lbs. tensile, per inch.
- To. 2. Weight per square yard, 10 oz.
Warp, cotton, 89 lbs. tensile (one inch wide).
Filler, goats' hair, 69 lbs. tensile (one inch wide).
- To. 3a. Weight per square yard, 9 oz.
Warp, wool, 49 lbs. tensile (one inch).
Filler, human hair, 47 lbs. tensile (one inch).
- To. 3b. Weight per square yard, 6 oz.
Warp, wool, 44 lbs. tensile (one inch).
Filler, human hair, 30 lbs. tensile (one inch).
- To. 4. Weight per square yard, 15 oz.
Warp, human hair, 67 lbs. tensile (one inch).
Filler, human hair, 84 lbs. tensile (one inch).

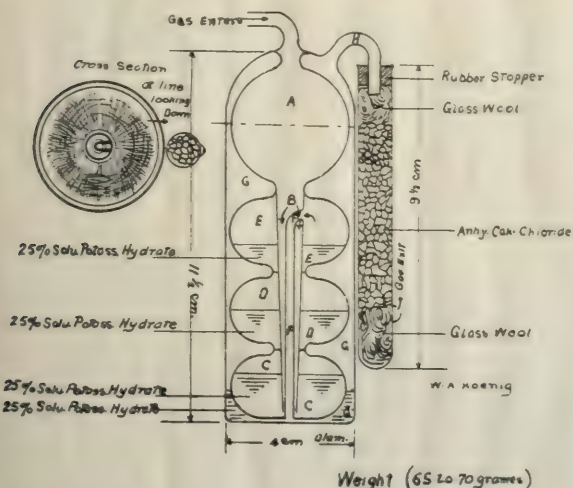
CHAS. P. FOX.

KOENIG POTASH BULB.¹

There are five advantages which this bulb has over the other bulbs thus far in use:

First.—Accuracy in cleaning at each weighing. All parts are easily accessible.

Second.—Accuracy in quick absorption. The bubbles bursting rapidly will not drive liquid over into



the calcium chloride tube and as the gas is washed several times instead of three it allows of more rapid circulation.

Third.—Amount of condensation surface is much less in this bulb.

Fourth.—Center of gravity on balance pan at each weighing can be found quickly and correctly.

Fifth.—Saving of time can be seen from the above and better on trial. The simplicity of the exposed parts make it less easily broken.

Description.—The gas enters at tube marked "gas enters," passes into A, then into tube B, through it and out at bottom into bulb C, squeezing through contraction up into B again, up into E, then passing into tube F (which is fused open on outside of tube B and open on outside of bulb C), down through F and out into the bottle G,G,G, passing through solution, then up and out through tube H into the calcium chloride tube which it leaves at opening marked "gas exit."

The instrument holds nearly twice as much KOH solution as the Mohr bulb, therefore will act for twice as many combustions without refilling. It weighs not over twenty grams.

To fill the instrument a piece of rubber tube is attached at H and KOH solution sucked in at tube marked "gas enters." To empty, the liquid is forced out at tube marked "gas enters" by blowing at tube H.

W. A. KOENIG.

MIDVALE STEEL CO.
PHILA

FILTERING RACK.

As any sugar-house chemist knows, the first few drops of a filtering solution shall be rejected. Letting these, generally turbid drops, first fall into the jars, often makes it very difficult to obtain a perfectly clear solution. With my rack I thought to simplify

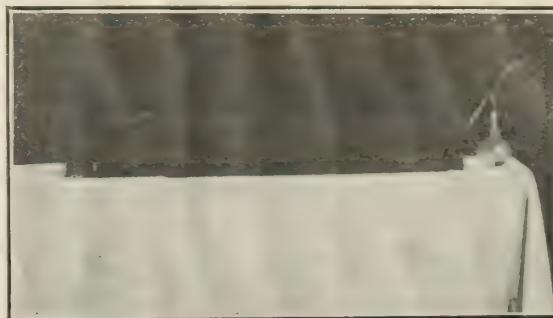


Fig. 1

the operations by preventing these turbid drops from getting into the jars.

Photo No. 1 shows the front of the rack, a stand for the filtering jars and a board for the funnels.

Photo No. 2 shows the back. Directly under the funnel board is seen an inclined gutter of a grade of about 2 per cent.; under the lower end of this is placed a receptacle.

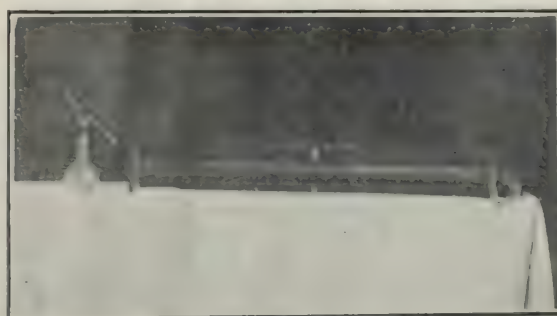


Fig. 2.

In operating, flasks, funnels and jars are put in their places; then the solutions are poured onto the filters, photo No. 3. The first parts of all the filtrates fall into the inclined gutter and flow into the receptacle.

If there be a series of samples, it will be found that by the time all the solutions are poured onto the

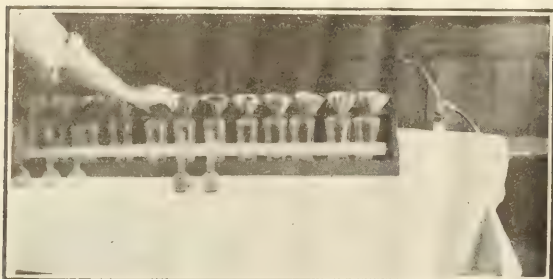


Fig 3.

filters, the first one is filtering perfectly clear and is ready to be transferred to its jar, as shown in photo No. 4.

The rack will be found convenient for another reason: When filling the polarization tubes, the funnels are put back into the corresponding holes in the funnel board, instead of being put on the jar previously used, as is generally done. In this way the solutions remain unaltered, and can be used



Fig 4.

again as a check, in case any doubt should arise about a reading on the polariscope.

The size of the rack can be increased or decreased at convenience. The one shown in the photographs has room for 12 samples.

ALFRED KRAFFT.

CHEMICAL LABORATORY
WAIALUA AGRICULTURAL CO., LTD.
WAIALUA, OAHU, T. H.

SAPONIFICATION OF FATS FOR TITER DETERMINATION.

Editor of the Journal of Ind. and Eng. Chemistry:

We notice the publication, in *THIS JOURNAL* for November, of an article in the "Notes" entitled "Rapid Saponification of Fats for Titer Determination," by C. V. Zoul, of the Proctor & Gamble Co., Cincinnati, O. We are very glad to see this method published, as we have long felt it should have more publicity as it is very reliable, and most convenient.

However, the article is worded so as to lead a reader to believe it is new and original with Mr. Zoul, as can be inferred from the first paragraph of the article,

also from his statement in the third paragraph: "Glycerine has been used for saponification but never for titers." If you will refer to a letter written to you by us, July 10, 1909, offering our cooperation to the Committee on Uniformity, you will find that we then enclosed you a copy of a method of glycerine saponification for titers which we suggested could be published in the "Notes" if you considered it of sufficient interest. The method was not published but in your letter of July 17, 1909, you stated that it and the soap-stock method accompanying it would be considered by the Committee on Uniformity.

Mr. Campbell, when chief chemist in 1900, first used the method for the titer test, adapting it from the Leffmann-Beam method of saponification for volatile fatty acid determination as given in Allen, 3rd edition, Vol. II, Pt. I, page 61. This method has been in daily use in our laboratory continuously and exclusively about ten years, and during that time we have handed it on to many others. Among these we may mention Mr. Oscar Wurster, chief chemist, The M. Werk Soap Co., Cincinnati, O., Mr. Robt. E. Divine, consulting and analytical chemist, Detroit, and Mr. Wm. E. Garrigues, chemical engineer of Detroit in 1907. We have noticed no mention was made of the method in the work on titer tests done by the Assoc. of Official Agricultural Chemists, Bureau of Chem., Bulletins 81 and 90, and from this assume that the method has not been in general use.

While we possibly may not claim to be originators of the application of glycerine saponification to titer tests, yet as we seem to have used the method more and longer than any one of whom we know, and as the method as published seems to be worded as if new and original, it seems to us only just that the matter be placed in the proper light before the readers of *THIS JOURNAL*.

Yours respectfully,

ARCHIBALD CAMPBELL,
C. P. LONG.

LABORATORY OF THE GLOBE SOAP CO.,
CINCINNATI, OHIO.

THE USE OF GLYCERINE IN SAPONIFYING FATS IN THE TITER TEST.

The following rapid method of saponifying fats for the determination of the titer has been worked out in this laboratory and is now being used for all titer determinations.

Fifty cc. of high-grade c. p. glycerine (97 per cent. glycerine) and twenty cc. concentrated caustic potash solution (100 grams KOH dissolved in 100 cc. distilled water) are placed in a liter flask and warmed gently on an asbestos board over a low flame. When hot, fifty grams of the molten fat are poured in and the flask rotated gently. Saponification begins at once and is soon complete, although there is usually some foaming before the mixture becomes clear. Complete saponification is shown by the mixture becoming perfectly clear and homogeneous. When saponification is complete the flame is removed and

five hundred cc. of hot water added, cautiously at first, to avoid excessive foaming. The flame is then replaced and sufficient dilute (1 : 3) sulphuric acid added to decompose the soap. A few minutes' boiling gives a clear layer of fatty acids. The acids are then washed and dried in the usual way. The process is quite rapid, clear acids being obtained in 20 to 25 minutes. The results show perfect agreement with standard methods.

The use of glycerine in the titer test was first suggested to the writer by Mr. R. R. Henley, Junior Laboratory Inspector in this Division.

The development of this method had been completed and its accuracy thoroughly tested when the paper entitled "Rapid Saponification of Fats for Titre Determination," by Charles V. Zoul, appeared in the November number of *THIS JOURNAL*.

The present note is offered as an independent confirmation of the rapidity and reliability of Mr. Zoul's method. His priority in demonstrating the value of glycerine for this purpose is, of course, conceded.

R. H. KERR.

FROM THE LABORATORIES OF THE BIOCHEMICAL DIVISION,
BUREAU OF ANIMAL INDUSTRY, U. S. DEPARTMENT OF
AGRICULTURE.

CANDELILLA WAX.

INSTITUTO MEDICO NACIONAL
7A DE BALDERAS, No. 94
Mexico, D. F.

Departamento de Quimica Industrial.

December 31st, 1910.

The Editor, The Journal of Ind. and Eng. Chemistry.

DEAR SIR:

The attention of this Department has been directed to articles recently published in your valuable periodical, contributed by Messrs. G. S. Fraps and J. B. Rather, and relating to "Candelilla Wax," and also to previous contributions by Messrs. Hare and Bjerregaard referring to the same subject.

Since it appears that the above-mentioned authors have overlooked the publication in the "Anales" of this Institute, of articles referring to this wax, since the time of its discovery in 1905 by Professor J. McConnell Sanders, chief of the Division of Applied Chemistry in this Institute, until the present year, we would ask you to kindly direct the attention of the above-mentioned authors and of your readers to a treatise recently published by the Educational Department of this Government, in which is included the botanical description of the Candelilla plant as classified by Prof. Gabriel Alcocer, curator of the herbarium, and a resumen of the chemical data obtained by Prof. McConnell Sanders.

In this resumen the chemical and physical constants of waxes from diverse territories in Mexico and from plants collected in different seasons of the year are compared, and the discovery of the hydrocarbon hentriacontane claimed by Messrs. Fraps and Rather is shown to have been anticipated by McConnell Sanders in the "Anales" for October, 1907.

As the exploitation of this wax has now become one of the National industries of this country, and

since its properties have attracted some attention in the commercial world, an English edition of the treatise above mentioned is in course of preparation, and a copy will be sent you as soon as published.

In the meantime we would ask you to kindly give the necessary publicity to this letter, for which courtesy we beg to anticipate our best thanks.

Remaining yours very truly,

Jefe del Departamento de

Quimica Industrial.

Editor, Journal Industrial and Engineering Chemistry:

Through an oversight of the printer and ourselves in our article "Some Imperfect Paving Bricks," *THIS JOURNAL*, Dec., 1910, we omitted to acknowledge the kind assistance of Dr. W. G. Brown, Professor of Technical Chemistry at the University of Missouri, in giving us the use of his apparatus and private laboratory, and for the many helpful suggestions and criticisms that he proffered during the course of the work. The work itself was suggested by him, and through his influence the authors obtained all the material necessary for the tests, and we wish to take this opportunity of expressing our appreciation.

JAS. C. LAWRENCE.

CHAS. J. BONER.

SCIENTIFIC AND INDUSTRIAL SOCIETIES.

DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS OF THE AMERICAN CHEMICAL SOCIETY.

MINNEAPOLIS MEETING, DECEMBER 30-31, 1910.

The meetings of the Industrial Division held at Minneapolis, December 30 and 31, 1910, were presided over by Arthur D. Little, *Chairman* of the Division. John White was selected as temporary *Secretary*.

The election of officers to serve during the year 1911 resulted as follows:

Chairman, G. C. Stone, 55 Wall St., New York.

Vice-Chairman, William Brady, 7642 Marquette Ave., Chicago, Ill.

Secretary, F. E. Gallagher, 93 Broad St., Boston, Mass.

Executive Committee, The Officers, The Editor of the *Industrial Journal*, *Ex-Officio*, and H. S. Minor, J. O. Handy, W. H. Walker, Clifford Richardson, G. E. Barton.

The Secretary's report was read and approved. The following abstracts are taken from this report:

"The enrolment in the Industrial Division is now 1040. The special work carried on by the Secretary since the last meeting has been largely directed towards the accumulation of data from the Industrial members leading to the publication of a descriptive directory of the members of the Division. For this purpose blank cards were mailed to all the members, and the returns have been satisfactory. We may consider, therefore, that the data is at hand for the proposed directory, and that it can be published as soon as funds are available for this purpose."

Only two of the Divisional Committees submitted reports for this meeting:

REPORT OF THE COMMITTEE ON DEFINITION OF INDUSTRIAL TERMS.

Your "Committee on the Definition of Industrial Terms" has the honor to report that it has continued its labors since

the San Francisco meeting, with results which are not entirely encouraging.

Definition of Bronze.—Attempts to define bronze have met with great opposition on the part of producers. It would seem that a large proportion of the material which is put upon the market as bronze is merely brass and contains no tin, and great objection has been raised to any attempts to change the designation of such material. It will not be listened to by producers unless legislation, similar to the Pure Food Law, should be enacted which would compel them to do so. The American Chemical Society could define bronze and brass with little difficulty, but such definitions would not be adopted industrially, for reasons which are too apparent to need mention. It would require an authority greater than that of the Society to impose such definitions on the producers. The policy to be followed in this respect must be decided upon by the Division. It has been suggested that the authority of the United States Government must necessarily be invoked to accomplish anything in this direction.

Definition of High-grade Inorganic Chemicals.—This sub-committee has been giving consideration to the proper definitions of the term "pure," "chemically pure" and "technical" as applied to high-grade inorganic chemicals. No definite conclusions have been reached up to the present time, but it is hoped that something may be arrived at at the meeting to be held in Minneapolis as a basis for further work.

The sub-committee reports that there seems to be in the minds of different manufacturers a desire not to give information to the committee, and until it can satisfy them that the work is for their benefit, it will be unable to come to any definite conclusions. It has been suggested that the aid of the Bureau of Standards at Washington be enlisted.

Definition of Heavy Chemicals.—This sub-committee reports that it has been unable to accomplish anything for the same reasons that have been met by the previous committee.

Definition of Pharmaceutical Products.—The chairman reports that it will be impossible for this committee to do anything until the appearance of the new Pharmacopoeia.

Definition of Iron and Steel.—The chairman of this committee reports that he has had a conference with the chairman of a similar committee appointed by the International Society for Testing Materials, the result of which is that they have arrived at the conclusion that very little progress can be made along this line at the present time, and they suggest that an effort be made to bring up the subject in 1912 at the 8th International Congress of Applied Chemistry, and at the meeting of the International Society for Testing Materials, and possibly the Iron and Steel Institute. A full discussion of this subject before some section at the meeting on one of these organizations might result in overcoming some of the difficulties which, at the present time, stand directly in the way of progress towards the adoption of any standard definition or nomenclature, as applied to the iron and steel industry.

Definition of Portland Cement.—Awaiting the results of the research on the constitution of Portland cement now being conducted by the Geophysical Laboratory of the Carnegie Institution, it would seem inadvisable to attempt to define Portland cement at the present time.

Definition of Petroleum Products.—At the present time it seems possible to go beyond the classification of these products presented in our last report, in view of the fact that commercial distillates from various petroleum vary in gravity for the same class of material, thus making any general statement of their density impossible.

Definition of Bitumen and Asphalt.—A meeting of a sub-committee of the American Society for Testing Materials, consisting of the same gentlemen composing the Committee of the

Division of Industrial Chemists, have not been able to arrive at anything satisfactory in this direction. Industrial influence, as in the case of bronze, has been the stumbling-block which has prevented agreement.

It appears that the attempt on the part of the Division to define "Industrial Terms" has met with such opposition that a satisfactory agreement upon anything, at the present time, will be impossible, but your committee hopes to pursue the subject in such a way that the resistance at present encountered may be overcome, but the prospect for immediate success does not seem promising.

An expression of individual opinion at the meeting at Minneapolis or to the committee would be of value, as well as suggestions as to any other industrial line in which an attempt may be made to define industrial products, in which there would be probability of success.

COMMITTEE ON DEFINITION OF INDUSTRIAL TERMS,

(Signed) CLIFFORD RICHARDSON,
Chairman.

REPORT OF COMMITTEE ON STANDARD SPECIFICATIONS.

The Committee on Standard Specifications regrets its inability to present a more complete report at this time.

Nine sub-committees have been endeavoring for the past six months to formulate specifications for the following materials:

Soda Ash	Muriatic Acid
Alum	Nitric Acid
Bleach	Turpentine
Caustic Soda	Solder
Sulphuric Acid	

Reports for the Minneapolis meeting were promised by four committees, but they have been obliged to disappoint us as it proved impossible to submit their data in proper form, and have requested an extension of time.

The Committee on Bleach completed its work and submitted a specification based upon the present trade custom of 35 per cent. of available chlorine. After carefully considering this, however, our committee felt that owing to the variable composition of bleaching-powder, provision should be made for purchasing bleach upon a unit basis, in much the same manner as caustic soda and other chemicals are bought. It has, for this reason, been deemed advisable to refer the matter back to the sub-committee.

The committee wishes to call to the attention of the Division the desirability of closer coöperation with other societies interested in these same lines in order to prevent duplication of effort and thus secure the greatest possible efficiency. This is especially advisable in the work of the committees on specifications and standard methods, since in many cases the drafting of a specification resolves itself into the selection of a standard method. Some plan of organization whereby the work on specifications and methods for this Society could be carried on jointly with that of other societies having committees engaged on similar subjects would in the opinion of the committee be decidedly beneficial. (Signed) HERVEY J. SKINNER,

Chairman.

Both of these reports were approved by the Division and it was also voted to continue all of the committees now at work.

After the reading of an important paper by P. H. Walker and F. W. Smither upon the subject of "Platinum," a committee was appointed, consisting of P. H. Walker, F. W. Hillebrand and a third to be selected by them, to consider the whole question of the Quality of Platinum Laboratory Utensils, and to report at the Indianapolis meeting. (E. T. Allen has since been selected as the third member of this committee.)

It is voted to make an assessment of \$1.00 per member upon the membership of the Division for carrying on the divisional work. Up to the present time the expenses of the Division have

been met entirely by the officers, the members never having been called upon to contribute to meet the expenses of the Division. An endeavor will be made during the next few months to publish the directory of members which has been compiled by the Secretary, and it is particularly for carrying on this work that the assistance of the members is required.

A vote of thanks was extended to the Bausch and Lomb Optical Company for the loan of a lantern during the meeting.

In the absence of the chairman, the temporary chairman, Mr. William Brady, upon motion appointed W. D. Richardson, S. W. Parr and John White to draft suitable resolutions expressive of the appreciation of the Division for the work which its first chairman, Arthur D. Little, has accomplished in organizing and building up the Division. This committee will report at the next general meeting of the Division and their resolutions will be embodied in the minutes of that meeting.

Subsequent to the business meeting the following papers were presented and discussed:

J. T. Donald. "An Improved Process for Finishing Beef Extract."

A. D. Smith. "Self-Recording Efficiency."

F. B. Porter. "Efficiency in Acid Phosphate Manufacture."

Walter P. Schuck. "Chemistry as a Factor in Foundry Efficiency."

Jas. C. Lawrence. "Note on the Utilization of Lumber Waste."

W. S. Williams. "The Use of Peroxide for Silk Bleaching."

C. F. Wood. "Economical Steam Generation."

C. M. Bullard. "The Importance of Eliminating Air Leaks in the Manufacture of Sulfite Acid."

S. W. Parr and F. W. Kressman. "The Spontaneous Combustion of Coal." (Illustrated by lantern.)

George P. Dieckmann. "The Modern Manufacture of Portland Cement from the Chemical and Mechanical Standpoint." (Illustrated by lantern.)

Harrison E. Ashley and Warren R. Emly. "Errors in Determining the Sizes of Grain of Minerals and the Use of Surface Factors."

Harrison Everett Ashley. "The Utilization of Smelter Smoke in Preparing Sulfates from Clays."

G. A. Abbott. "The Determination of Water in Mixed Paints."

A. H. Sabin. "Linseed Oil."

Harry McCormack. "A Modified Process for Cane Sugar Manufacture."

G. W. Thompson. "The Importance of a Standard Temperature for Specific Gravity Determinations and for Standardizing Standard Measurements."

Percy H. Walker and F. W. Smither. "Platinum Laboratory Utensils."

J. K. Clement. "The Work of the Chemical Laboratories of the Bureau of Mines."

W. D. Richardson. "Experiments on the Corrosion of Iron."

John White. "The Determination of Moisture in Coal."

Charles P. Fox. "Tensile Strength of Hair Cloth."

The following papers were read by title:

H. W. Rohde. "Notes on the Production and Composition of Mexican Pulque and Mescal."

H. C. Hamilton. "Soaps from Different Glycerides. (Their Germicidal and Insecticidal Values in Themselves and When Mixed with Active Agents.)"

Wm. M. Barr. "The Disintegration of Concrete in Septic Tanks."

Geo. C. Whipple and Melville C. Whipple. "The Solubility of Oxygen in Sea Water."

Geo. L. Heath. "The Exact Electrolytic Assay of Refined Copper. 1. Standard Method. 2. In Solenoid with Revolving Electrolyte."

Geo. L. Heath. "The Determination of Arsenic and Antimony in Copper, including a New Rapid Volumetric Method."

In addition to those on the regular program the following papers were presented:

Perry Barker. "Fuel Costs."

B. T. Babbitt Hyde. "Determination of a Basis for the Compensation Allowance to Employees."

H. E. Mills. "Methods of Rubber Analysis."

Mr. F. G. Heuchling, Efficiency Engineer for the Chicago Civil Service Commission, read by consent of the Division a paper on the work of the commission, especially in their efforts to bring about greater efficiency on the part of their employees.

A letter was read from Mr. H. A. Schwartz, Chairman of the local Publicity Committee, inviting all members to attend the Indianapolis meeting of the American Chemical Society in the summer of 1911.

F. E. GALLAGHER, *Secretary*.

AMERICAN CHEMICAL SOCIETY. DIVISION OF FERTILIZER CHEMISTS.

MINUTES OF MINNEAPOLIS MEETING, DECEMBER 30, 1910.

Meeting called to order by Chairman, F. B. Carpenter.

Minutes of last meeting read and approved.

On motion it was decided to have the papers read first.

The following papers were read:

1. Chairman's Address, F. B. Carpenter. "The Results of Soil Investigations as Affecting the Use of Fertilizers."

2. J. M. McCandless. "A Bacteriological Method for Determining Available Organic Nitrogen."

3. J. M. McCandless. "Uniform Rules and Regulations for the Admission of Ammoniates Throughout the Southern States."

4. J. E. Breckenridge. "Availability of Organic Nitrogen."

5. Charles S. Cathcart. "The Use of Nitrate of Soda in Commercial Fertilizer."

Reports of the following committees were made:

Phosphoric Acid by G. Farnham, *Chairman*. Report received and accepted.

Potash by J. E. Breckenridge, *Chairman*. Report received and accepted.

Nitrogen by P. Rudnick. Report received and accepted.

Legislation Committee by A. Lowenstein, *Chairman*. Report received and accepted.

Phos. Rock Com. by C. F. Hagedorn. Received and accepted.

On motion Nominating Committee for officers for 1911 was appointed by *Chairman*: P. Rudnick, G. Farnham, A. Lowenstein.

Committee reported the following:

P. Rudnick, *Chairman*,

J. P. Street, *Vice-Chairman*,

J. E. Breckenridge, *Secretary*.

Executive Committee:

F. B. Carpenter,

A. Lowenstein,

W. J. Jones, Jr.,

G. Farnham.

The above were elected.

Availability of Organic Nitrogen was referred to Nitrogen Committee.

Publishing of Proceedings of meeting was referred to Executive Committee.

Many important subjects were discussed.

On motion meeting adjourned.

J. E. BRECKENRIDGE, *Secretary*.

CO-OPERATIVE WORK ON PHOSPHORIC ACID BY THE DIVISION OF FERTILIZER CHEMISTS OF THE AMERICAN CHEMICAL SOCIETY, 1910.

Letter Accompanying Samples:

Two samples are being mailed you. No. 1 Acid Phosphate, No. 2 Acid Phosphate, blood, bone, tankage, peat and potash. There is also a sample of Standard Ammonium Citrate being sent by express. The sample of citrate which was prepared by Dr. W. J. Jones has been sterilized. It has been found that when sterilized the citrate does not undergo any changes.

You are requested to determine insoluble phosphoric acid

equal volume of water, as a check. Bring solution to sp. gr. 1.09 by weight at 20° C.

Determine ammonia as follows: Measure 25 cc. of the citrate solution at 20° C., in duplicate, into 250 cc. graduated flasks and bring to volume at room temperature. Place 25 cc. of these solutions into 500 cc. Kjeldahl flasks, dilute to 350 cc. with distilled water, add NaOH or MgO and boil until the distillate measures 300 cc., the distillate being caught in $N/2$ acid, titrate excess acid and calculate ammonia to grams per liter.

A large number of solutions prepared in this way have been found to vary between 43.5 and 43.7 grams of NH_3 per liter.

RESULTS OF THE CO-OPERATIVE WORK OF THE PHOSPHORIC ACID COMMITTEE OF THE AMERICAN CHEMICAL SOCIETY.

Analyst.	Moisture,		Standard citrate.				Analyst's citrate.				Time for filtering and washing (min.).	
	Sample No. 1.	Sample No. 2.	Grams NH_3 per liter.	Ins. P_2O_5 Sample No. 1.	Ins. P_2O_5 Sample No. 2.	Filter paper.	Grams NH_3 per liter.	Ins. P_2O_5 Sample No. 1.	Ins. P_2O_5 Sample No. 2.	Filter paper.	Sample No. 1.	Sample No. 2.
T. S. Gray, Jacksonville....	43.61	43.54
	9.22	4.80	43.75	0.88	4.40	589	43.61	0.96	4.23	589	30	2 h. 45 min.
A. G. Stillwell, New York...	0.87	4.93	5.04
	43.60	0.90	4.89	43.70	0.95	5.06
	1.01	5.07
F. B. Porter, Atlanta.....	10.46	5.76	43.80	0.86	4.56	45.50	0.83	4.27
	10.44	5.82	43.80	0.96	4.46	45.50	0.92	4.37	3	4
	44.00	45.20	0.88	4.55
	0.90 ¹	4.60
C. S. Warner, Cincinnati....	11.35	7.42	44.08	0.80	4.08	44.43	0.80	4.16	15	30
	0.68	4.08	Purp	5	5
J. Q. Burton, Atlanta.....	9.90	5.01	43.66	1.01	4.86	43.57	0.94	4.83	13	2 1/2 hrs.
	10.01	5.02	43.66	1.02	4.89	43.60	0.93	4.79	10-15	...
	0.46 ²	0.59-0.59
	0.46-0.63 ²
Stillwell & Cladding, N. Y. .	9.67	4.95	43.67	0.77	4.40	43.78	0.74	4.59	10	10
W. D. Richardson by	9.74	5.41	44.54	0.64	3.90	43.60	0.76	3.63	20	20
E. F. Scherubel, Chicago..	9.66	5.65	...	0.50	3.70	0.79	3.82
L. Watling, Cincinnati.....	10.30	5.90	43.40	1.00	4.50	43.40	1.00	4.50	25	2 1/2 hrs.
J. E. Breckenridge, Carteret	0.62	4.85	0.65	4.95
W. J. Jones, LaFayette.....	9.43	4.65	43.52	0.92	4.53	597	43.50	1.03	4.55	597	2-3	8-10
	9.58	4.46	43.52	0.85	4.38	597	43.50	...	4.44	597
	9.80	...	43.52	0.83	4.50	590	43.50	0.82	4.45	590	3-5	10-30
	43.52	0.85	4.53	590	43.50	1.03	4.52	590
	43.52	1.03	4.57	589	43.50	4	25
	43.52	...	4.62	589	...	0.79	4.62-4.67	575	30	46
	43.52	44.59	0.96	4.54	597	2	12 ⁵
	4.64	4 ⁵
	42.48	0.99	4.07	597	2 1/2	12 ⁵
	4.29	9 ⁵
G. Farnham, Cincinnati....	9.6	4.72	43.80	0.88	4.65	44.08	0.85	4.84
	9.9	4.53	43.80	0.83	4.65	44.10	0.82	4.73	4	25
F. B. Carpenter, by	10.2	5.51	...	0.83	...	589+589 ³	...	0.81	...	589+589	18	...
H. G. Lewis, Richmond....	0.87
	0.85
	0.87	...	589 ⁴	...	0.88	...	589	50	...
	4.60	597 ⁴	4.47	5-6 hrs.
	4.12	597+597 ³	4.00	597+597	...	35-50

¹ Citrate sol. prepared by method in THIS JOURNAL, 1, 618.

² 9 cm. funnel used which allowed some of the insoluble to pass through. Previous results by same analyst where 5.5 cm. funnel was used gave brilliantly clean filtrates.

³ Glass funnel with platinum cone.

⁴ Washed once on Hirsch funnel.

⁵ Contents of flask were poured on filter. After liquid was drawn off the filter and contents were removed to another funnel, covered with an unused filter paper and washing continued.

only, using the standard citrate and also a citrate solution prepared as follows:

Place 300 grams of citrate acid in porcelain dish, add 600 cc. distilled water to partially dissolve the acid and then with constant stirring, one liter of 0.96 ammonia until acid is dissolved. Make solution alkaline to litmus paper with 0.96 ammonia and allow to stand 24 hours in open dish out of contact with laboratory fumes.

Next make neutral by the official alcoholic calcium chloride method. The filtrate from the alcoholic calcium chloride precipitate is made neutral to one drop of $N/10$ acid or alkali using cochineal as indicator. Place the filtrate diluted with an equal volume of water in a Hessler jar and use a second jar containing the alcoholic calcium chloride, also diluted with an

The analytical method is intended to solve as a check on the alcoholic method. Report number of grams of NH_3 per liter in the standard citrate solution, also in your solution.

In weighing portions for analysis pour entire sample on piece of glazed paper, mix thoroughly and draw sample from different parts, mix after each weighing.

Moisture.—Take 2 to 5 grams and heat until weight is constant at 100° C.

Washing.—Place 2 grams on 9 cm. filter paper and wash until neutral to litmus.

Digestion.—Place 100 cc. citrate in 200 or 250 cc. flasks, either Erlenmeyer or round bottom and have level of water in bath at least one inch higher than liquid of flask. Run a blank with a thermometer in flask, since it has been found that the

water in bath will have to be kept at 66 to 67 degrees in order that citrate solution may be at 65°; shake blank same as regular flask and agitate water in bath each time flasks are shaken. Remove flasks from bath promptly at end of half hour.

Filtration.—Use a Hirsch or Buchner funnel having a perforated bottom of at least 2½" diameter, with suction. Use S. & S. 590 or similar grade of paper with sample No. 1 and S. & S. 597 with sample No. 2. (Paper should be exactly same diameter as perforated bottom.) Pour off the citrate solution first, before allowing the paper pulp to clog filter. Wash with small portions of water at 65° C., using about 30 cc. at each washing. Wash six times after entire contents of flask have been placed on filter. Report length of time required for filtering and washing.

Solution.—Make solution by any of the official methods.

Precipitation.—Determine p205 by the official gravimetric method. At this point run a blank on your reagents, using double the quantity of reagents and divide the result by two. Report individual determinations not averages, also blank.

You are respectfully asked to follow instructions closely, as the Committee thinks that the value of coöperative work in the past has been considerably lowered by the analyst not following instructions closely enough. Unless this is done results are not comparable.

If for any reason you find it impossible to follow instructions kindly mention any change of methods in your report.

Reports should be sent to G. Farnham, cr. The Jarecki Chemical Co., Cincinnati, Ohio, on or before the expiration of one month from the time samples are received.

Thanking you for your valued coöperation and with every assurance that same is greatly appreciated by

The Committee on Phosphoric Acid:

G. Farnham, *Chairman*,
J. Q. Burton,
W. J. Gascoyne,
W. J. Jones,
J. R. Powell.

AMERICAN CHEMICAL SOCIETY, DIVISION OF FERTILIZER CHEMISTS. POTASH COMMITTEE WORK FOR DECEMBER MEETING, 1910.

Letter accompanying samples:

A sample of fertilizer has been sent you marked "Official Potash Sample, A. C. S. for December meeting 1910."

Will you test it by the following methods?

Potash.—Method 1: Official method for water-soluble potash as stated by the A. O. A. C., U. S. Dept. of Agr., Bureau of Chemistry, *Bulletin 107*, allowing solution having had the ammonia and ammonium oxalate to stand only long enough to cool before filtering, not over four hours, or stating in your report the time the solution stood before filtering.

Method 2: Weigh 2 grams on to a 11 cm. filter paper and wash with small portions of hot water (as near boiling as possible) into a 200 cc. flask, allowing each washing to run through before adding the next, until about 175 cc. are in the flask. Add to washings in the flask about 2 cc. HCl (conc.), heat to boiling, add ammonia and ammonium oxalate as usual, cool at once, make to mark and filter. Proceed as in official method, evaporating at least 50 cc.

Moisture.—Make moisture determinations in duplicate according to your usual method, specifying what weight was taken, how long drying and what kind of an oven was used and inside temperature of oven.

General Remarks.—Use Gooch filter for potash and wash the potassium platonic chlorid off the filter with hot water and reweigh the filter.

Kindly make report in full reporting all tests and not averages, and give any experience in potash work which you care to relate.

Send report to J. E. Breckenridge, Carteret, N. J., by June 1st.

Thanking you for whatever work you can do in this line.

Committee on Potash:

J. E. Breckenridge, *Chairman*,
F. B. Porter,
E. L. Baker.

RESULTS OF CO-OPERATIVE WORK IN POTASH, DIV. FERTZ. CHEMISTS.

	Meth. No. 1.	Av.	Meth. No. 2.	Av.	Dif. in favor Meth. No. 2 plus.	Mois. av.
E. L. Baker, N. Y. Exp. Station, Geneva, N. Y.	9.99		10.50		0.50	
J. A. Bizzell, Cornell Univ., Ithaca, N. Y.	9.98	9.99	10.48	10.49		17.69
E. O. Thomas, 812-814 Paul - Gale - Greenwood Bldg., Norfolk, Va.	10.13		10.24		0.12	
Carlton C. James, Pac. Guano & Fert. Co., Honolulu, Hawaii.	10.15	10.14	10.28	10.26		16.73
Filtered after ½ hr. cooling.	10.30		10.09			
Stillwell & Gladding, 181 Front St., N. Y. City.	10.23	10.27	10.04	10.07		16.99
Filtered after 2 hrs. cooling	9.97		10.20		0.14	
P. K. Nisbet, Am. Ag. Chem. Co., North Weymouth, Mass.	10.01	9.99	10.06	10.13		18.52
H. D. Young, Univ. of Cal., Whittier, Cal.						
Method No. 1 filtered after 1 hr. cool.	9.86		10.11		0.10	
H. B. Battle, 103 S. Court St., Montgomery, Ala.	9.90	9.88	9.85	9.98		17.29
Three ½, 2½ and 2 hrs. standing. No difference.						
Geo. W. Miles, 29 Central St., Boston, Mass.	10.20	10.20	10.28	10.28	0.08	16.62
E. W. Gaither, O. Ag. Exp. Station, Wooster, O.	10.16	10.16	10.31	10.31	0.15	16.81
W. P. Colvin, Kansas City, Kas.	10.13		10.54		0.31	
Three hrs. before filtering.	10.17		10.40			
F. A. Nantz, Box 17, Little Rock, Ark.	10.13		10.54			
One hr. before filtering.	10.20	10.16	10.41	10.47		17.16
F. B. Carpenter, Mr. Henry, Vir. Car. Chem. Co., Richmond, Va.	10.32		10.38		0.10	
F. L. Parker, 40 Broad St., Charleston, S. C.	10.33		10.44			
W. H. Whitthouse, Moosic, Pa.	10.33	10.33	10.47	10.43		17.25
A. Lowenstein, Morris & Co., Chicago, Ill.	9.95	9.95	10.31	10.31	0.36	17.05
R. S. Norris, Exp. P. Station, work done by S. S. Peck.						
F. R. Werthmueller, W. J.	10.11		10.20		0.13	
A. E. Jordan, and R. S. Norris. N.	10.12	10.12	10.30	10.25		17.08
J. S. Burd, Univ. of Cal., Berkeley, Cal.	10.14		10.44		0.15	
½ hr. before filtering	10.28		10.44			
0.5 gram used	10.22	10.21	10.20	10.36		16.84
2 1 gram used	10.22		10.34		0.13	
	10.22	10.22	10.36			
				10.35		17.08
	10.13		10.20		0.02	
	10.17	10.15	10.13	10.17		17.22
	9.98		9.92			
	9.92	9.95	9.93	9.93		16.75
	10.05	10.05	10.32	10.32	0.27	16.90
	10.19	10.19	10.36	10.36	0.17	17.04
	10.12		10.35		0.14	
	10.21	10.17	10.27	10.31		16.93
	10.18¹		10.39¹			
	10.21¹		10.43²			
	10.26²		10.35¹			
	10.24²		10.45²			
	10.25²		10.43¹			
			10.53²			
			10.42¹			
	10.23	10.46²	10.43	0.20		16.71

RESULTS OF CO-OPERATIVE WORK IN POTASH, DIV. FERTILIZER,
CHEMISTS (Continued).

	Meth. No. 1.	Av	Meth. No. 2.	Av.	Dif. in favor. Meth. No. 2 plus.	Mois. av.
B. L. Hartwell, R. I. State College, Kingston, R. I. F. S. Hammett.	10.51	10.51	10.46	10.46		16.95
F. B. Porter, Swift Fert. Works, Atlanta, Ga.	9.93		10.50		0.43	
	10.00		10.40			
	10.01		10.48			
	10.08		10.44			
	10.12	10.03	10.50	10.46		17.15
W. C. Dumas, A. M. Lloyd, Lab., Atlanta, Ga. 1/2 before filter.	10.38		10.41			
	10.22	10.30	10.55	10.48	0.18	
48 hrs. before filtering.	10.20	10.20				
2 months later.	10.40	10.40				16.82
B. W. Bangs, Am. Ag. Chem. Co., Carteret, N. J.	10.12	10.12	10.46	10.46	0.34	17.21
Average for whole.		10.16		10.31		17.04
B. W. Bangs, Am. Ag. Chem. Co., Carteret, N. J.	10.12	10.12	10.46	10.46	17.21	17.21
Average for whole.		10.16		10.30		17.04

Remarks.—Cobalti Nitrite Method (Volumetric), 10.04 and 9.94 per cent. F. B. CARPENTER.

The filter papers and contents after washing in Method 2 were found to contain 0.04 per cent. potash by Method 1.

Tests by Method 1 were not allowed to stand over $\frac{3}{4}$ hours before filtering.

All the official samples were made by mixing 5800 gms. of acid phosphate and 1200 gms. muriate of potash analyzing; potash A. O. A. C. method acid phosphate 0.09 K_2O muriate 60.16 K_2O .

Percentage K_2O by theory 10.39.

In mixing and bottling, the samples undoubtedly lost enough moisture to account for Method 2 running slightly higher than that calculated. F. B. PORTER.

REPORT ON MOISTURE ON POTASH SAMPLE, DEC., 1910, MEETING A. C. S.

Name.	Wt. in gms.	Time in hrs.	Temp.	Moisture.
E. L. Baker.	2	9	Constant	100°
J. A. Bizzell.	2	5	Water oven	97
E. O. Thomas.	2	5		99
E. O. Thomas.	6	days after first set.		1st
Carlton C. James.	5	5		2nd
Stillwell & Gladding.	10	5	Water oven	99
Stillwell & Gladding.	5	5	Water oven	99
H. D. Young.	4	4	Water oven	98.2
H. B. Battle. Watch glasses	4	4	Air oven	105
Geo. W. Miles.	4			99.5
F. A. Nantz.	2	2	Air oven	105
F. B. Carpenter.	2	5	Water oven	97
F. L. Parker.	5	5	Air bath	98-100
W. H. Whitehouse.	2	5	Steam bath	95-105
A. Lowenstein.	5	5		105
J. S. Burd. P. L.	2	5	Constant	100
Mc Creary.				16.62
B. L. Hartwell.	2	6	Water oven	98
F. B. Porter.	10	5		100-105
F. B. Porter.	10	5		100-105
P. K. Nisbet.	5	5		100
E. W. Gaither.	2	5		100
E. W. Gaither.	2	5		100
W. P. Colvin, diff.	5-10	6	Constant	105
W. P. Colvin, diff.	5-10	6	Constant	105
R. S. Nossis	2	5		100-105
Double Watch Glasses	2	5		
	2	5		
	2	5		
W. C. Dumas	5	5		99
W. C. Dumas	1	5		99
W. C. Dumas	1	5		99
B. W. Bangs.	5	5		100

Moisture Remarks No. 3.—Moisture determinations were made in an oven with a water jacket, the inside temperature of which was 98° C. Two samples of 2 grams each were heated for four hours, showing a loss of 0.3382 and 0.3368 gram. Upon heating for two subsequent hours, the total loss was 0.3386 and 0.3386. Further heating showed that the weights had become constant.

BURT L. HARTWELL.

10 gms. in a shoe blacking box dried 5 hours at 100 to 105° C. Thermometer bulb near box in oven.

Oven No. 1.—10 × 12" double wall oven with reflux condenser using glycerine solution between walls. (E. & A. No. 3030).

Oven No. 2.—8 × 10" single wall oven heated by single burner underneath. (E. & A. No. 3030).

Oven.	No. 1.	No. 2.	Calculated.
Moisture in 5 hrs. at 100-105°.....	17.29	16.74	15.95
	17.16	17.34	
Total moisture shown after 3 additional hrs. at 130°.....		19.11	19.32
		19.33	

The moisture tests at 130° were made to see whether the difference between the calculated and determined figures would still obtain at that temperature. It seems that the potash releases some of the moisture at 100° that would without its presence be shown only at higher temperatures.

F. B. PORTER.

Remarks.—Proposed Method 2 gives more potash than official method, and approaches nearer theory.

Inasmuch as this method includes nothing but potash soluble in water and from the fact that the referee on potash of the A. O. A. C. reported same results it would seem that Method 2 gave better results than the official method.

J. E. BRECKENRIDGE.

REPORT OF THE COMMITTEE ON FERTILIZER LEGISLATION OF THE DIVISION OF THE FERTILIZER CHEMISTS OF THE AMERICAN CHEMICAL SOCIETY.

To the Executive Committee and Members of the Division of Fertilizer Chemists:

Your committee begs to report that their attention has been given largely to the subject of organic ammoniates in mixed fertilizers. Attached herewith are copies of correspondence on this subject among members of this committee and between this committee and the chairman of this division and the members of the committee made up of officials having in charge fertilizer inspection in their several states. This latter committee sent out a notice in March of 1910, which is attached hereto.

It will be noted in the circular above referred to that this committee contemplates publishing the solubility of the organic nitrogen in all the brands of commercial fertilizers examined, determined by a uniform method, and beginning this work with fertilizers examined on and after March 1, 1911. A sub-committee consisting of Mr. C. H. Jones, Chairman, Mr. J. P. Street, of Connecticut, and Mr. Burt Hartwell, of Rhode Island, have undertaken the study of a uniform method which is to be employed.

The chairman of this division and also the chairman of this committee wrote to Dr. Jones, chairman of this sub-committee, advising him of our interest in the matter and offering to cooperate if it should appear to be desirable to the sub-committee. As will be noted in Dr. Jones' letter, he states "that the matter of sending samples to others than those having fertilizer inspection directly in charge in the New England states has not been definitely settled. It is quite probable, however, that all interested parties will have a chance to take part in the work, and when things are ready, I will correspond with you further." Up to the present time, nothing further has been heard from Dr. Jones.

Inasmuch as there has been considerable controversy among agricultural chemists as to the value of the different methods for the determination of the availability of organic ammoniates, it would appear advisable that this matter be very carefully studied, and it is further recommended by this committee that the Committee on Nitrogen or a new committee be appointed, to study the methods for the determination of the availability of organic nitrogen in commercial fertilizers, either by itself or in coöperation with the Association of Official Agricultural Chemists, the above referred to a committee of New England chemists and other organized bodies making a study of this same subject.

Respectfully submitted,
A. LOWENSTEIN.

REPORT OF THE COMMITTEE ON PHOSPHATE ROCK.

The progress of the work of the Committee on Phosphate Rock has been seriously delayed by the fact that the routine duties of most of the members are heaviest at this time of the year. Considerable progress has been made, however. The committee has been organized into sub-committees on Moisture, Phosphoric Acid, Iron and Alumina, and each sub-committee has drafted tentative methods covering its individual branch of the subject. These tentative methods have been sent out to all the members of the committee together with carefully prepared samples of phosphate rock. Some of the members have been able to accomplish considerable work, others, through no fault of their own, have been absolutely unable to begin their work on these samples and methods.

It is therefore not possible to do more than make this report of progress at present. Such results as have been received seem to bear out the opinion held by many chemists at the present time that all the various methods are not equally well adapted to all varieties of phosphate rock. It is, however, not feasible to quote any specific data resulting from the work done so far in support of this view. This should not be understood to mean that the committee is trying to formulate different methods, each of which shall apply only to certain varieties of rock. Every effort will be made to develop a method which shall be equally applicable to all commercial varieties of rock and produce results which shall be exact enough for commercial work.

Another important subject is the matter of standard samples. Preparations have been made and work is well under way towards the standardization of one or more samples of phosphate rock which shall be available to those interested at a nominal cost. This involves not only a careful preparation of a large supply of an absolutely uniform sample, but also the development of scientifically accurate methods of analysis, so that the exact composition of the rock may be determined. After this has been done, such standard samples will be of the greatest service in testing the methods for commercial work developed in the meantime in the work of this committee.

C. F. HAGEDORN.

AMERICAN CHEMICAL SOCIETY. DIVISION OF PHARMACEUTICAL CHEMISTS.

The Division of Pharmaceutical Chemists of the American Chemical Society held its Minneapolis meeting in the Chemistry Building of the University of Minnesota on December 29th. The address of Prof. A. B. Stevens, *Chairman*, upon Pharmacopoeial Standardization was especially interesting and timely since Prof. Stevens is a member of the Committee of Revision, and Chairman of the Sub-Committee on Proximate Assays. The address outlined the work being done by the sub-committee mentioned and made clear the thoroughness and carefulness

with which the Pharmacopoeia is being revised. The new and improved methods of committee work were also explained.

The Report of the Committee on Quantitative Methods gave a résumé of the analysis of mercury salts by six different methods. The committee has done valuable work and is being continued. The report, although merely a report of progress, was ordered published in order that the greatest benefit may be obtained from the work of the committee.

The papers read at the meeting were as follows:

A. B. Stevens. "Citro Compounds of Iron."

E. R. Miller and G. H. Marsh. "Camphor in Oil of Sassafras."

L. E. Sayre. "Assay of Gelseminum."

F. Klein. "Rapid Determination of Sulphuric Acid with the Porous Clay Crucible."

E. Kremers. "Chemical Problems suggested by the Cultivation of Medicinal Plants. (1) Stramonium."

The following officers were elected for the ensuing year:

B. L. Murray, *Chairman*,

A. D. Thorburn, *Vice-Chairman*,

F. R. Eldred, *Secretary*.

Members of Executive Committee:

A. B. Stevens,

L. F. Kebler.

Yours very truly,

B. L. MURRAY, *Chairman*.

ABSTRACT OF REPORT OF THE COMMITTEE ON QUANTITATIVE METHODS.

Division of Pharmaceutical Chemists of American Chemical Society.

Your committee begs to offer the following report of work which has been done since the last meeting (July, 1910). In the search for suitable assays for the various mercury salts included in the U. S. P., for which a standard of purity is laid down and no assay process is given, investigation was made of a number of existing methods as indicated below.

In order that you may know the method of working of the committee, we give an outline of the plan pursued in this case. The chairman sent out requests to the members of the committee for suggestions as to methods suitable for general application to mercurous and mercuric salts. After going over the suggestions received, the following methods as proposed were again submitted to the committee, together with samples of mercurous chloride and mercuric iodide. The methods as submitted are as follows:

Method 1.

Suggested by Mr. L. A. Brown.¹

Applicable to mercurous iodide, chloride, bromide, and mixtures of mercuric and mercurous salts.

Weigh out sample of about 0.5 gram, place in Erlenmeyer flask of about 300 cc. capacity, add 10 cc. potassium iodide solution containing 2 grams KI; rotate and quickly add 50 cc. N/10 iodine solution by means of a pipette, agitate until all of the sample is in solution. Then run in N/10 Na₂S₂O₃ solution until all the free iodine has been removed, using starch solution if desired.



By mixing the HgCl with the solution of the potassium iodide immediately before adding the iodine solution, the insoluble salt goes into solution more quickly.

Method 2.

Suggested by Mr. L. A. Brown.²

Applicable to mercuric chloride, iodide, cyanide, nitrate, oxide, ammoniated mercury, metallic mercury, and preparations of mercury such as ointment of mercury, ammoniated mercury,

¹ See Schimpf, "Volumetric Analysis," p. 408.

² Merck's Report, 1908, p. 57.

nitrate, oxide solution of mercuric nitrate, Donovan's solution, plaster of mercury, etc.

Dissolve one gram of the sample (e. g., HgCl_2), using one or two grams of potassium iodide if necessary, in sufficient water to make 100 cc. of solution.

Take 20 cc. aliquot, add 1 gram KI, 5 to 10 cc. of 10 per cent. KOH sol., and 10 cc. of water containing 2 or 3 cc. of formaldehyde solution. Mix thoroughly and place on water-bath for about 10 minutes, or until supernatant liquid settles clear; then decant off through a small filter, washing residue with two portions or more of water, decanting off through filter as before.

Dissolve the small amount of metallic mercury off the filter by means of a few drops of hot diluted nitric acid (1:1), washing the filter with a few cc. of water to remove all traces of mercury. Collect filtrate and washings in the beaker containing the Hg, adding more nitric acid if necessary to secure solution of the mercury. Evaporate to about 2 or 3 cc. on a water-bath, then dilute with water and transfer to a 100 cc. flask, rinsing out beaker with successive amounts of water sufficient to make 100 cc. of the solution.

Take an aliquot representing about 0.100 gram of HgCl_2 , add 25 cc. of water, then a slight excess of 5 per cent. iodic acid solution, 5 cc. being enough. This is added drop by drop, agitating all the while to secure complete agglutination of the curdy precipitate. As soon as the supernatant liquid is clear, filter and wash precipitate with three or four portions of water.

Dissolve precipitate off the filter with a few drops of diluted HCl, wash filter thoroughly, add 1 or 2 grams of KI, allow to stand for about 5 minutes, then titrate the liberated iodine with $N/10 \text{ Na}_2\text{S}_2\text{O}_3$.

Each cc. of $N/10$ thiosulphate = 0.0022405 gram HgCl_2 .

In the case of ointments such as official ointments of mercury and its salts, remove the ointment base by means of the proper solvent, dissolve the residue with nitric acid, and apply the method as given.

Method 3.

Suggested by M. B. L. Murray.¹

Applicable to solutions of mercury nitrate, the mercury oxides, metallic mercury, mercury with chalk, and possibly some of the other mercurial preparations.

Not applicable to calomel or corrosive sublimate.

Those preparations of mercury as found in the U. S. P., which can readily be brought into solution in nitric acid, are satisfactorily assayed for mercury by electrolysis.

The sample may well be of such a size that the final weighing of the metallic mercury will show a weight of about 0.250 gram. The mercury solutions, or the dried preparations dissolved, are acidulated with 3 cc. of concentrated nitric acid, diluted to 125 cc., heated to 70° C. and then electrolyzed with a current of $N. D._{100} = 0.06$ ampere and two volts. The metal will be fully precipitated in from 2 to 4 hours, and may appear as a uniform metallic coating upon the platinum dish, which is used as a cathode, or it may appear in shiny droplets. After the deposition of the material is complete, the mercury is washed with water, then with alcohol, then with ether, and finally dried a short time in the desiccator and weighed. The electrolyte remaining may be tested qualitatively for mercury to show that the deposition was complete.

The time may be materially shortened by the use of the rotating anode and mercury cathode.

Method 4.

Suggested by Mr. F. O. Taylor.²

A solution of the mercury salt, containing about 0.2 gram of mercury in 25 to 50 cc. of solution, is treated with excess of

KI so that the HgI_2 formed redissolves. Render alkaline with NaOH; treat with 3 cc. of 40 per cent. formaldehyde solution diluted with 10 cc. of water and let stand with occasional stirring for about two minutes. Acidify with acetic acid; add 25 cc. of $N/10$ iodine and after all the precipitated mercury has combined with the iodine, titrate the excess with $N/10$ sodium thiosulphate solution.

Mercurous salts must be converted into mercuric before precipitation.

In the case of mercuric cyanide, sulphuric acid should be used instead of acetic in order to decompose any cyanogen iodide which may have formed.

Method 5.

Suggested by Mr. F. O. Taylor.¹

Estimation of Mercury as Arsenate.—The mercury must be present as a mercuric salt, and preferably as a nitrate, as the mercuric arsenate is not precipitated from the chloride solution. A small amount of free nitric acid does not interfere with the accuracy of the results. To a cold solution containing about 0.25 gram Hg in 100 cc. add 20 cc. of saturated solution sodium arsenate. The heavy yellowish white precipitate of mercuric arsenate immediately forms and settles rapidly, but for greater accuracy the author of the method recommends that the solution stand for several hours; then filter through a Gooch filter, wash thoroughly with cold water and dry at 100°.

Method 6.

Suggested by Mr. F. O. Taylor.¹

Estimation of Mercury as Chloride.—To a solution of the mercuric salt, preferably in the form of a nitrate containing about 0.25 to 0.4 gram Hg, add a slight excess of a mixture containing one drop of hypophosphorous acid to each cc. of H_2O_2 , and then immediately an excess of solution sodium chloride. Let stand for one hour, filter off the precipitated HgCl_2 , wash thoroughly, dry at 100° and weigh.

Below, in tabular form are given the results obtained by different members of the committee in using these methods.

ANALYSIS OF MERCUROUS CHLORIDE.

Chemist.	Method		Special method, Per cent. (e).
	Method No. 1 Per cent.	No. 4. Per cent.	
Mr. L. A. Brown.	100.10 (a)		
	99.91		
Mr. B. L. Murray.	98.94 (b)		99.62 (e)
	99.33		99.79
	99.25		
	99.35		
	99.23		
	99.19		
Mr. L. D. Havenhill	100.46 (c)	99.84	
	99.71	100.04	
	100.01	99.62	
	100.04	99.84	
Mr. F. O. Taylor.	100.18		
	(d)		

COMMENTS.

(a) Method is entirely satisfactory if closely adhered to.

(b) Method worked well although some time was consumed in effecting solution in iodine.

(c) The factors seemed too large to permit of sufficient accuracy when working upon samples of close to 100 per cent. purity.

(d) (Mr. Taylor's results are unfortunately unavailable, but his comments are at hand.) The chief difficulty with this method is the dissolving of the mercury by the iodine solution, which is very often extremely slow. Aside from this the method seems very good.

(e) Samples were dissolved in sodium sulphide solution and

¹ See Smith, "Electro-Analysis," pp. 90 and 94.

² See E. Rupp, *Berichte*, **39**, 3702 (1906); also *Chem.-Zeit.*, **34**, 229 (1910).

¹ See C. J. Pretzfeld, *Jour. Am. S. S.*, **1903**, p. 198.

electrolyzed $\frac{3}{4}$ hr. with 0.5 ampere, 4.5 volts, using mercury cathode and rotating anode.¹ Results very satisfactory.

ANALYSIS OF MERCURIC IODIDE.

Chemist.	Method No. 2. Per cent.	Method No. 3. Per cent.	Method No. 4. Per cent.	Method No. 5. Per cent.	Method No. 6. Per cent.
Mr. L. A. Brown	95.74(m) Highest of several		99.67 (l) 100.39		
Mr. B. L. Murray.	79.17(n) 86.36 81.50 86.04 62.01 80.82	98.68 99.38 98.52	98.57(u) 99.38		
Mr. L. D. Havenhill.	94.40(o) 94.19 94.65 91.88 97.65(f) 98.80(f) 97.65(f) 91.88(g) 93.95(g)	97.83 (i)(h) 97.94(h) 99.89(k) 98.86(k) 99.58(s) 99.98(t) 99.80(t) 99.70(t) 99.62(t) 100.50(t)	64.1 (p)(v) 98.64(r) 97.64(r) 98.80(s) 98.86(s) 99.98(t) 99.80(t) 99.70(t) 99.62(t) 100.50(t)	97.85(x) 93.10 98.09 94.00	97.98 97.84 97.60 97.51
Mr. F. O. Taylor.	(a)	(i)	(u)	(y)	(z)

NOTES.

- (f) Precipitating and washing in dilute alcohol.
 (g) Same solution as preceding (f) but washing with water.
 (h) Dried at 50° C.
 (k) Dried in desiccator room temperature.
 (p) 30 seconds with stirring for reduction.
 (r) 2 minutes with stirring for reduction.
 (s) 4 minutes with stirring for reduction.
 (t) 5 minutes with vigorous shaking.

COMMENTS.

(m) Mr. L. A. Brown, I got very poor results due possibly to two causes: (1) Mechanical loss of mercury in filtering after reduction. (2) Part of the mercury appears to come down in a colloidal condition and is lost in the filtrate. I have proven to my entire satisfaction that the reduction by formaldehyde in alkaline solution is quantitative, and what makes me believe that part of the mercury is in a colloidal form is that a *perfectly clear filtrate* will show the presence of mercury by hydrogen sulphide if completely saturated.

(l) Contrary to previous observations I find this method to give good results if the reduction is carried out in the cold and not allowed to stand too long before adding iodine solution. If the reduced mercury is allowed to coalesce and form large globules the solution of the mercury in the iodine solution is very slow.

(u) Mr. B. L. Murray, in using this method we found that two minutes was not sufficient time for the reduction of the mercury by formaldehyde. Even five minutes was too short a time and a little heat was used to complete the reduction; but this we found reduced the mercury to such a condition that it was very hard to dissolve in the iodine solution.

(n) The method gave us uncertain results.

(o) Mr. L. D. Havenhill, the amount of water used in washing the precipitate of mercury iodate tends to vary the results.

(i) Our work seems to indicate that there was a considerable loss of mercury, due to volatilization when the cathode was dried at a temperature of 50°.

(v) We found the time for reduction to be insufficient, also the stirring. Better, or at least higher results were obtained by vigorously shaking the mixture. The quantity of acetic acid used is indefinite. Our results, which are not herein reported, seem to show that the more acetic acid used, the lower

are the results. We believe that the size of the factor is too large to permit of sufficient accuracy when working on samples that run close to 100 per cent. in purity.

(x) In this method the mercuric iodide was reduced with formaldehyde in the manner indicated by the method of E. Rupp, dissolved in nitric acid and precipitated with sodium arsenate. It was noted that the precipitate of mercuric arsenate was not of uniform color, and the higher results here reported were materially whiter in color than the lower results which were more yellow in color.

(q) Mr. F. O. Taylor, we find this method inaccurate because of the distinct solubility of the mercuric iodate in water, which solubility may be proved by testing the filtrate from the mercuric iodate by hydrogen sulphide, when a very decided test for mercury can be obtained.

(j) Unquestionably the electrolytic method is extremely accurate when used by one who is experienced and has at hand the proper apparatus, and it can also be made a very rapid method. It does not seem, however, to be suited to the requirements of pharmacopoeial estimation, as at the present time one is much more likely to find the requisite skill and apparatus for making other forms of assay than the electrolytic, among those to whom these assays would be chiefly valuable.

(w) Here again the difficulty of dissolving the precipitated mercury in iodine solution is the chief drawback. With care the method can be made accurate, but it usually requires more time than a process of this kind should.

(y) Inaccurate results here may be attributed to the slight solubility of mercuric arsenate in water, which seems to be sufficient to render the method not very desirable.

(z) No careful work was done by me on this method, but only some preliminary tests, and it would appear that special care must be taken in the reduction of the mercuric salts and it is therefore preferable to use phosphorous acid instead of hypophosphorous acid.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

THIRD ANNUAL MEETING, NEW YORK, DEC. 7-10, 1910.

The Officers of the American Institute of Chemical Engineers elected at the Third Annual Meeting in New York, December 7 to 10, 1910, are as follows:

President, Dr. F. W. Frerichs, Herf and Frerichs Chemical Company, St. Louis Mo.

Vice-President, George P. Adamson, Vice-President and General Manager, The Baker and Adamson Chemical Co., Easton, Pa.

Eugene Haanel, Director of Mines, Dept. of Mines, Ottawa, Ont., Can.

Dr. Leo. H. Baekeland, Yonkers, N. Y. Research Chemist and Chemical Engineer.

Secretary, Prof. John C. Olsen, Polytechnic Institute, Brooklyn, N. Y.

Treasurer, Henry S. Renaud, 159 Front St., New York.

Auditor, Herbert Hollick, Camden, N. J.

Ex-Presidents, Dr. Samuel P. Sadtler, Dr. Chas. F. McKenna.

Directors. H. F. Brown, Wilmington, Del.

Ludwig Reuter, Berkeley, Cal.

Thorn Smith, Detroit, Mich.

J. T. Baker, Phillipsburg, N. J.

Dr. W. M. Grosvenor, New York.

Richard K. Meade, Allentown, Pa.

William M. Booth, Syracuse, N. Y.

Edward G. Acheson, Niagara Falls, N. Y.

Prof. Edward Hart, Easton, Pa.

The American Institute of Chemical Engineers has voted to award a gold medal to the author of the best original contribution to the literature of applied chemistry, such contribution

¹ THIS JOURNAL, 2, 481.

to be presented only to the American Institute of Chemical Engineers with provisions as follows:

1. Members and non-members may compete.
2. The paper must be mailed by registered post to the secretary of the Institute, John C. Olsen, Polytechnic Institute, Brooklyn, N. Y., at least sixty days prior to the semi-annual meeting in June, 1911.
3. The papers will be examined by the Committee on Publication, of which William P. Mason, Rensselaer Polytechnic Institute, Troy, N. Y., is Chairman.
4. The first announcement of the award shall be made by the President of the Institute at the semi-annual banquet when the honor will be conferred.
5. If, in the judgment of the committee, no paper presented is worthy of the proposed honor, the award will not be made.
6. The first medal presented shall be given to the author of the best paper which shall have been presented to the Institute from its organization up to within 60 days of the next meeting. Subsequent medals shall be given for papers presented during the year.

A Medal Committee has been chosen to solicit funds for this purpose. The members of the committee are:

Samuel P. Sadtler, 39 South 10th St., Philadelphia, Pa.,
Joseph W. Richards, Lehigh Univ. South Bethlehem, Pa.,
Andrew D. Robertson, 2 North 9th St., Richmond, Va.,
Wm. M. Booth, *Chairman*, 710 Dillaye Bldg., Syracuse, N. Y.

It is proposed to raise by subscription Twelve Hundred and Fifty Dollars (\$1250.00). This is to be invested for the Institute and shall be known as a "Medal Fund," the interest of which is to be used for the award. Any person or corporation may contribute. Any subject for investigation and report may be suggested. However, all moneys received will become a part of the general fund set aside for this purpose.

The members of the committee feel that some very valuable papers will be presented and that one of the main aims of the Institute will be accomplished, "to publish and distribute such papers as shall add to classified knowledge in chemical engineering and shall increase industrial activity."

Abstracts of papers read before the American Institute of Chemical Engineers at its Third Annual Meeting, Dec. 7 to 10, 1910:

FITZGIBON BOILER.

JEROME ALEXANDER.

This paper gives a brief description of the construction and operating principles of the Fitzgibon boiler, a type combining vertical with horizontal tubular features. The boiler is internally fired, and is entirely without external or internal brick work, thus avoiding the annoyance and expense of repairs at inopportune times. A heavy asbestos or magnesia covering reduces radiation below that found in ordinary bricked-in boilers. The boiler is a quick steamer, economical in coal consumption, and can be easily moved about.

EVOLUTION OF PORTLAND CEMENT PROCESSES.

DR. CHAS. F. MCKENNA.

The paper of the retiring president was a rapid review of the history of Portland cement from the day of Asdin's invention, portraying particularly the different stages in the process from the crude method of Asdin's to the modern process of burning in rotary kilns and the fine pulverizing. The economy of the present day is such that for one cent twelve pounds of raw material can be taken from the earth, dried, ground, calcined and vitrified and the product ground again.

Considerable attention is paid to the old forms of wet processes, and the statement is made that present-day European practice in grinding to a semi-wet slurry hard materials, not marls,

is the most important advance in modern times, and should be taken up more vigorously in America. The basis for this is the claim that the drier expense is saved, finer incorporation is obtained, better clinkering and easier grinding of the clinker. The critical feature of the modern semi-wet process is to secure the maximum of fineness of slurry with the minimum water. It is said that in good practice some materials can make with less than 35 per cent. of water a slurry which can be pumped, and as it dries in the upper end of the long kiln the extra coal consumption is not marked. Modern rotary kiln practice, particularly the long kiln, is touched upon, and the use of pre-heated air from clinker kilns and diminished indraft of cold air.

SEWAGE DISPOSAL IN EUROPE.

RUDOLPH HERRING.

Disposal of sewage by dilution was first practiced. Of the sixteen largest cities in the world having a population of over one million inhabitants, every one without exception now employs the dilution method, where flowing water is available and a sufficient quantity of oxygen is dissolved in it, to represent a flow of fresh water equivalent to at least 3 cubic feet per second for every thousand persons discharging sewage.

Where a water supply is taken from a river, it must be purified even after any sewage entering above has been treated.

Where a river is not used as a water supply sewage may contaminate the food, fish, oysters, etc. The commercial value of such food is insignificant compared with the cost of removing all the conditions that would impair their hygienic qualities. It is therefore much cheaper to take them at a greater distance from the large cities where no dangers exist.

The nuisance to sight produced by sewage is almost everywhere in Europe prevented by keeping all plainly visible floating matter out of a river by screening. Screens with a mesh as small as one millimeter are used.

A nuisance to smell is prevented by constructing sewers with such smooth interior surface and good grade as will deliver the sewage practically fresh to the outfall and insure an immediate submergence of the sewage as far below the surface of the water as possible. This method is entirely successful in many continental cities.

The amount of sewage discharged into the Thames is so regulated that the dissolved oxygen in the water does not generally fall below 30 per cent. of saturation. No nuisance results under these conditions.

European experience justifies the conclusion that purification of sewage by the oxygen in flowing water is entirely satisfactory.

Sand purification of sewage requires the delivery of the sewage in fresh condition and a preliminary separation of the coarser suspended particles after which the finely divided matter may be oxidized in intermittent sand filters. The more recent developments involve improvements on the septic tank method of purification. Dr. Imhoff has developed a tank having two compartments. In the upper the suspended matter settles out and is drawn off through a slot. In the lower compartment the sewage is decomposed with the evolution of methane, carbon monoxide and dioxide. No sulphuretted hydrogen is produced. The decomposition is complete in from three to six months. The sludge which is removed dries quickly to a friable material similar to garden mold. The annoying question of the disposal of sewage may therefore be considered satisfactorily settled.

PRINCIPLES OF SEWAGE DISPOSAL.

GEO. C. WHIPPLE.

The basic principles underlying all methods of sewage disposal are to get rid of sewage without danger to the public health, with the least possible nuisance to the smallest number of people, with the least damage to property and at the smallest cost.

The process of purification is usually carried on in several

stages: First, a partial removal of the suspended matter by screening or sedimentation or both, second, a process of oxidation using sprinkling filters, contact beds or sand filtration, and third, a final removal of bacteria by sand filtration or disinfection.

The term "sewage purification" is popularly applied to any or all of these processes. This has contributed not a little to confusion of ideas. Laymen innocently suppose that when sewage is "purified" it becomes pure, whereas the sanitary engineer may mean only that it is purer than it was before. How much purer depends upon the method used. It would be of decided benefit to the question of sanitation if more definite terms were used, such as sewage clarification, oxidation, deodorization, disinfection, filtration, etc.

The chief danger from sewage is the contamination of public water supplies. For the protection of public water supplies it is not safe to depend upon sewage purification works alone unless more than ordinary precautions are taken, for the reason that most of the processes cannot be depended upon to remove bacteria from the sewage to a sufficient extent, while with the combined system in use complete purification is impossible. Sewage purification is of advantage as it offers a second line of defense, and increased factor of safety. It also serves to prevent nuisances to sight and smell, which are of real damage to property and affect personal comfort. Sewage works themselves, however, may be the cause of similar nuisance.

What appears to be needed in this country at the present time is some method of coöperation by which needed sanitary reforms can be brought about at least expense. It is unbusiness-like to compel the purification of the sewage of a large upstream city in order to protect the water supply of a small city lower down, provided pure water can be furnished the latter in some better and cheaper way. Legislation that clothes the state authorities with power to prevent the pollution of sewage but does not give them power to compel the purification of water or to control pollution by trade wastes is unfortunate. It naturally leads to litigation rather than coöperation and may retard rather than hasten necessary sanitary reforms. If our state authorities cannot be trusted in this matter it may be that a proper solution of the difficulty will be found in the establishment of District Boards similar to those in England and Germany, such Boards having jurisdiction over the limits of particular water-sheds. In some respects these natural hydrographic boundaries have advantages over artificial state boundaries. In the near future also our national government will doubtless take a hand in the matter. In whatever form the authority may be constituted the idea of coöperation should prevail, and ironclad rules against steam pollution should give way to a rational distribution of the burden of purification of both water and sewage, and an equitable adjustment of cost made between the parties interested, thus decreasing the total expense of sanitary measures required, and utilizing natural resources for the purification of sewage in water as far as this is safe.

If the system of water carriage of sewage continues in use the time will some day come when the sewage of all of our cities will be purified, partially or completely, and all surface water supplies filtered. It is proper to anticipate this consummation as far as our means permit, but meantime it is good business and sound common sense to spend our money first where it will go furthest and do the most good, building water filters and sewage purification works, sometimes one, sometimes both, as they may be needed.

Adequate remedies against stream pollution from the standpoint of nuisance have been usually obtained by an appeal to the principles of common law. Cases involving bacterial pollution by sewage have been thus far too few to establish definite precedents. It will be interesting to see whether, in view of

our increasing population, and especially the increasing growth of our cities, the courts will ultimately decide that the use of unfiltered river water as a source of water supply by riparian owners is a reasonable use of the water.

The writer is optimistic in regard to the improvements that are being made in methods of sewage disposal. He believes that the near future is to see extensive developments in the art. Important as are the recent improvements in the technical details still more important and necessary is a rational assignment of the means employed to the work at hand. The use that is to be made of the water into which sewage is discharged and the conditions tending to natural purification are to be studied with greater minuteness than ever before; the method of dilution is to be used more rationally, and the designs of the sewage disposal plants made to fit more closely the particular conditions. The general result will be the construction of more and simpler plants for the treatment of sewage, and where occasion makes necessary, the installation of yet more efficient devices for bacterial purification than those now employed.

MANUFACTURE OF HYDRATED LIME.

RICHARD K. MEADE.

Hydrated lime is mechanically slaked lime. Just the correct portion of water is added so that the resulting product is a dry fluffy powder. Most of the hydrated limes on the market up to a few years ago were very crude products, usually containing considerable carbonate. Now, however, processes have been perfected which produce a lime consisting almost entirely of the hydrate. The process for the manufacture of hydrated lime usually consists of three stages: (1) crushing the lime, (2) mixing the lime and water, and (3) separating the hydrate from the unhydrated portion. In some processes instead of separating the hydrate from the unhydrated portion, the two are ground together in some form of pulverizing mill.

The hydrating plant itself is usually located adjacent to the lime kilns. The lime is drawn from the kilns and is immediately crushed in some form of rotary or pot crusher. From this it is conveyed mechanically to the hydrator, in which the slaking is done. There are several forms of this latter in use but all come under two heads, continuous hydrators and batch hydrators. The continuous hydrators most used is the Kritzer hydrator, which consists of a number of cylinders mounted one above the other on a steel frame work. Through the middle of each cylinder runs a shaft to which are fastened paddles. The lime is fed in at the upper cylinder and mixed with the water. The paddles stir it up and also force it to travel through the cylinder. It then drops into the next cylinder and here it is mixed up and passed on by the paddles in this and so on until it has passed all of the cylinders. The proportions of lime and water are determined by means of an automatic feed for the lime and a valve for the water.

The Clyde hydrator is a batch hydrator in which the lime and water are weighed in separate charges consisting of about 1500 pounds of lime and the proper amount of water for this much lime. The pan rests upon a ball bearing and is revolved by means of a gear and pinion on the under side of the pan, which is surmounted by a hood and a stack. Plows running across the surface of the pan are fastened to a stationary frame-work above the latter. The lime and water are fed into the hydrator through an opening in the side, and the plows stir it up and mix the two. When hydration is completed, the lime is discharged through an opening in the center of the hydrator, which during the mixing is closed.

After passing through either hydrator, that portion of the lime which has been slaked is in the form of a very fine fluffy powder, all of which will pass through a very fine sieve. Mixed in with this, however, are always some unslaked lime, unburned limestone and silicious ores. For the better grades of hydrate

it is usual to separate out this foreign material by means of screens, although where the amount of these constituents is small they are sometimes ground in with the hydrate. Fuller, Lehigh and Raymond Mills are principally used for the grinding, while the separators most used are the Newaygo and the Columbian.

The packing of the hydrate is best done in cloth (100 lbs.) or paper (40 lbs.) bags automatically by means of the Bates system which consists of a valve bag and machine for filling the same. The bags are provided with a valve and are tied before being filled. This valve is made by ripping, folding and sewing one corner of the bag. The cement is inserted through the valve by means of a tube on the bagging machine which automatically fills and weighs the bag. The machinery for hydrating magnesian lime having a capacity of 2 to 3 tons per hour costs about \$5000 and for high calcium limes \$12000. The cost of hydrating lime is about 25 to 30 cents per ton. One ton of lime, however, will often make more than one ton of hydrate.

The advantages of hydrated lime are: it is a fixed product and does not deteriorate with age; it can be handled without risk of fire; it may be shipped by water and packed in cloth or paper bags; it can be used for all purposes for which lime is used and is more convenient than the latter. In addition to this it can be used for mixing with cement for which purpose quicklime cannot be used.

BLEACHING OF OIL WITH FULLER'S EARTH.

DAVID WESSON.

The literature of fuller's earth and its application is very meager. It appears to be first mentioned about 1889. From the best information obtainable fuller's earth was first used for bleaching fats and oils in Chicago on a large scale about 1878, or 1880, although it is said to have been used for a long time previous in Northern Africa for clarification of olive oil.

The first application was very cumbersome, the earth being stirred into the hot oil and allowed to settle, after which the oil was decanted and the residue boiled with water and pressed.

The filter press was first used between 1880 and 1882. The efficiency of a given sample of fuller's earth cannot be readily determined by chemical analysis. The best method is by making a bleach test on a small scale. In comparing the bleaching properties of two earths they should always be passed through sieves of the same size in order to obtain an accurate comparison.

Fuller's earth doubtless owes some of its bleaching properties to the presence of a certain amount of water of constitution. This, if driven off by either drying of the earth or by adding it to oil of too high a temperature, will prevent bleaching.

The reason why fuller's earth seems to bleach is not positively known. Fuller's earths differ greatly in their absorptive properties and show great differences in their liability to spontaneous combustion.

The arranging of filter plants is a matter of considerable importance. The place for filters is on the top of a refinery under suitable shelter. By having them at an elevation above the bleach tanks, oil can be allowed to run back to the same, or can be fed to any part of the building, or run easily to storage by gravity; besides, the fire risk is much less, and when the filters are steamed out the nuisance of the steaming is entirely done away with.

The mixing kettles for oil and fuller's earth are practically cylinders provided with mechanical agitation and suitable heating coils.

Filter pumps should be slow-moving, capable of working up to a pressure of 150 to 200 lbs. The operation of filter plant is quite simple. The earth is mixed with the oil at the proper temperature and then pumped through the filter press, the first portions of the oil being allowed to run back to the mixing

kettle, or bleacher, as it is often called, until it comes up to the required standard, after which it runs directly to storage.

UNSOLVED PROBLEMS OF SEWAGE DISPOSAL.

C. E.-A. WINSLOW, Associate Professor of Biology at the College of the City of New York, and Curator of Public Health at the American Museum of Natural History.

The three main ends of sewage treatment, the elimination of suspended solids, the oxidation of organic matter and the destruction of pathogenic bacteria can all be attained by practically efficient methods but there are minor difficulties to be overcome in each case. The pathogenic bacteria can be destroyed when necessary by disinfection with bleaching powder but the dosing devices available for use in small plants are very defective. The oxidation of organic matter can be economically effected by the use of sand, contact or trickling beds. Distribution systems for trickling filters require further study. The intermittent sand filter has possibilities of intensive action not attained in plants operated at present largely at haphazard. It is the accumulation of suspended solids on the surface which keeps the capacity of sand beds down to 100,000 gallons per acre per day and experiments carried out at the Sewage Experiment Station of the Massachusetts Institute of Technology show that the rate can be raised to 200,000 or 300,000 gallons if suspended solids are removed by careful preliminary treatment. Sludge disposal is still the most serious of the unsolved problems of sewage treatment. It has been minimized at the Technology Experiment Station by the use of a deep tank on the septic principle, but so operated that the sewage rises and washes the sludge continually, and thus keeps it from becoming overseptic. By this means the liquefying process is so accelerated that over 70 per cent. of the deposited total suspended solids have been liquefied. The utilization of sewage sludge though not yet economically realized furnishes promising possibilities to the industrial chemist in the future.

SEWERAGE AND SEWAGE DISPOSAL IN NEW YORK AND VICINITY.

GEORGE A. SOPER, PH.D., M. Am. Soc. C. E. and President Metropolitan Sewerage Commission of New York.

For the most part, the sewage of New York is conveyed in crude condition by the shortest route to tide water and discharged at or near the surface of the water. There are over 500 sewer outlets discharging 600,000,000 gallons of sewage per day. In all parts of the harbor above the Narrows, the water is seriously polluted and rendered objectionable both to sight and smell. Along 175 miles of shore the water is so polluted as to be dangerous to bathe in. These conditions will rapidly become worse as the population increases.

A standard of purity for the water of New York harbor has been proposed by Col. Black and Prof. Phelps as a result of studies, estimate and apportionment. They consider that the dissolved oxygen in the water should not fall below 70 per cent. of what would be present if the water did not receive any sewage. This limit has already been exceeded.

A definite plan and program of main drainage, including outfall works and purification plants designed to improve the present unsanitary conditions, has been proposed by the Metropolitan Sewerage Commission. The study of carrying out this plan so far as New York is concerned has been entrusted to this commission. This work is now progressing satisfactorily.

SANITARY CONDITIONS IN THEIR RELATION TO THE WATER SUPPLY IN THE VICINITY OF NEW YORK.

NICHOLAS S. HILL, JR.

This paper calls attention to the very unsatisfactory condition of the water supply in the suburbs of New York and

emphasizes the fact that health conditions in New York City are very materially affected by sanitary conditions in the suburbs. The suburban territory adjacent to New York which is considered includes Northern New Jersey and Westchester County. It is shown that the very great growth of population in New Jersey tends to pollute the natural water supplies and on the other hand creates an increasing demand for a supply of pure water. In order to provide for this future demand, means should be taken at once to prevent further contamination of the New Jersey streams and to abate the nuisances already existing along these water courses.

Similar conditions prevail in Westchester County. The location of a large number of institutions in this county, such as sanitariums, hospitals, orphan asylums, etc., further tend to pollute the water-sheds. In many of the smaller towns there are no sewage disposal systems of any kind whatever. The remedies to be applied are proper sewage disposal and filtration of water supply.

It is impossible for a number of scattered communities to undertake the abatement of nuisances, the proper disposal and filtration of the water supply.

The necessary state supervision to procure efficient sanitary protection, under existing laws and with the funds at present at the disposal of the State Department of Health, is difficult to obtain. Pennsylvania appropriates Two Hundred Thousand (\$200,000) Dollars per year and New York, Eighty-five Thousand (\$85,000) Dollars.

Storage reservoirs of suitable size cannot be built because in a thickly populated section, like the one under consideration, the presence of villages and towns in valleys suitable for storage purposes makes the cost of condemnation excessive. Railways and highways also traverse reservoir sites in many cases. Such costs can be incurred only by large cities like New York. In other cases, a pure supply of water can only be obtained from Connecticut which will result in interstate complications if such sources must be largely drawn upon.

It would seem as if it would be necessary to organize a Metropolitan Water Board under whose direction a considerable supply of pure water and the enforcement of sanitary relations could be provided for these scattered communities. Otherwise New York City must be depended upon to arrange to furnish water in the necessary quantities to towns and villages immediately north of it, especially as the Metropolis has pre-empted the most available streams, namely the Croton, Byram and the Bronx.

WESTERN SOCIETY OF TECHNICAL CHEMISTS AND METALLURGISTS.

After a career of six years the Western Association of Technical Chemists and Metallurgists has disbanded, and its journal, *The Western Chemist and Metallurgist*, published its last issue in December, 1910. Started as a little society in Denver, local sections were added in other parts of Colorado, in Utah, Montana, South Dakota and Mexico, and a volume of some four hundred pages was printed annually. With the lapse of time there came the disintegration due to a lack of interest on the part of the members—a lack of interest due partly to the nomadic habits of men connected with the mining and smelting industries, which renders anything like a permanent local membership next to impossible, and partly to the fact that the burden contributing to the journal fell on only a few of the members, and they could not with reason be expected to supply enough material to keep a technical journal up to the highest standard. The following extracts from a letter by President W. D. Engle are self-explanatory.

"To the Members of the Western Association of Technical Chemists and Metallurgists:

"For the past two years the Board of Control of your Association has endeavored to work out some plan whereby the original

plan of the organization might be carried out more successfully. The original plan contemplated a strong organization of western and metallurgical chemists publishing a journal which would afford a means of exchanging ideas and make possible a comparison of methods and plans of work which would be of advantage to all. To some degree this has been realized, but not to that degree that will justify us in continuing.

"In Denver there has been, from the first, a strong section. However, outside of Denver it has been difficult, if not impossible, to arouse and maintain the desired enthusiasm,

"The disbandment of the Association is a source of much regret to many of us. . . . The members of the Board are a unit in the desire to keep up the organization, but they are equally a unit in deciding that we must disband unless we can maintain the present degree of efficiency and have good prospects of making a stronger society and a larger and better journal.

"We have gained much in the way of recognition by other societies and scientific authorities . . . and our journal is frequently quoted. It seems a waste that what has been gained must be abandoned, but we must not start a new year without good prospects of being able to complete it. It therefore becomes my disagreeable duty to announce to you that this will be the last issue of the journal, and that the end of the present year will close up the career of the Western Association of Technical Chemists and Metallurgists."

BOOK REVIEWS AND NOTICES.

Die Aetherischen Oele. By E. GILDMEISTER AND FR. HOFFMANN. 2nd edition by E. GILDMEISTER. Vol. I. 8vo. pp. viii + 697. Laboratory tables in pocket. 1910. Miltitz bei Leipzig: Schimmel and Co.

Gildmeister and Hoffman's work on the essential oils has long been one of the few books on this important subject. It has been well known and favorably received. The present second edition in two volumes by Gildmeister in conjunction with the firm of Schimmel will be welcomed. The general arrangement of the present edition is similar to that of the first. Since the publication of the latter, Semmler's great work in four volumes on the constituents of the essential oils has been completed. This work and the many researches of Wallach, Tiemann and others during the intervening years afford a foundation for a great extension of the part devoted to the components of the ethereal oils, and this part of the book covers 286 pages. The book is divided into four parts: 1. Historical, 258 pages; 2. Winning of Perfumes, 26 pages; 3. Components, 286 pages; 4. Testing, 100 pages. The historical chapters are very commendable, covering the spice trade in ancient times and during the middle ages, the general history of essential oils, history of special oils, and history of distillation. The methods of chemical and physical testing are adequate and excellent. The text and illustrations are well printed and the whole is well indexed.

Schimmel and Co's. Semi-Annual Report for October, 1910, contains some 204 pages $5\frac{1}{4} \times 7\frac{3}{4}$ in. It contains the customary commercial and scientific review of the principal essential oils, descriptions of new essential oils and about 50 pages devoted to recent research work concerning terpenes and terpene derivatives.

"Cement Age" and "Concrete Engineering" Consolidated.—Cement manufacturers, engineers and chemists will be interested in the announcement that *Cement Age*, of New York, and *Concrete Engineering*, of Cleveland, two of the leading monthly publications in the cement field, have been consolidated. *Cement Age*, which was established in 1904, has been issued under the editorship of Mr. Robert W. Lesley, Vice-President of the American Society for Testing Materials, and an associate of the American Society of Civil Engineers, who is also one of the most prominent figures in the cement industry in this country. *Cement Age* has covered the popular features of cement construction, as well as the engineering and manufacturing side of the industry, and *Concrete Engineering* has been especially devoted to that branch of the industry indicated by its title. Beginning with the January, 1911, issue, the two magazines will be consolidated under the title "*Cement Age* with which is combined *Concrete Engineering*." The magazine will be slightly larger than the present size of *Cement Age*, and will have a type page 6 X 9 inches, thus retaining the distinctive magazine form which has been a popular feature of the older publication. The increased space will be more acceptable to both readers and advertisers. A two-column make-up will be a further innovation.

It is the purpose to preserve the best features of both the magazines, thus maintaining the prestige each has won. The use of cement from the architectural and engineering standpoints, as well as its manufacture, will be thoroughly covered, together with the popular features that are of such great interest to the general public.

Allen Brett, editor of *Concrete Engineering* for the past two years, will take the position as associate editor of the new publication, and Arthur E. Warner, formerly business manager of *Concrete Engineering*, will become the western manager. There will be no change in the present staff of *Cement Age*, Mr. Lesley continuing as editor, Frederic F. Lincoln as president of the Cement Age Company, in charge of the New York office at 30 Church Street and of the eastern advertising field, and Edward A. Trego as associate editor.

The *Mining World Index* conducted by the *Mining World* will mark an important inauguration in mining periodical literature. It aims at no less a project than to systematically index each week all the current periodicals and other literature relevant to any branch of the mining, mining engineering, metallurgical, and mineral and rock products industries. The value of this bibliographic work to technologists is self-evident.

RECENT INVENTIONS.

The following patents relating to Industrial and Engineering Chemistry are reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., Washington, D. C.

Only a few patents which are deemed of greatest importance are abstracted in this department.

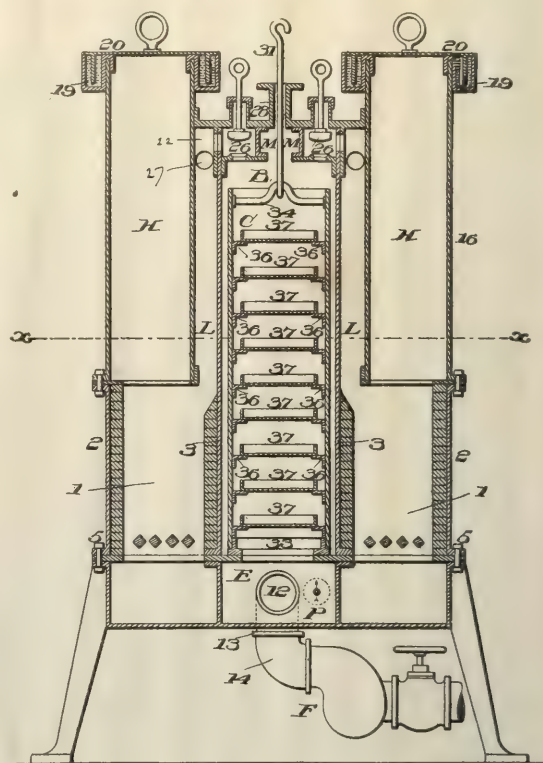
Abstracts of all patents appear regularly in *Chemical Abstracts*, to which publication the reader is referred.

977,992. Process for the Recovery of the Paraffin Ingredients from Cannel-Coals. HENRY WURTZ, Newark, N. J.

To obtain all hydrocarbon ingredients of cannel-coal, and

other similarly constituted materials, and to recover them in a chemically unchanged condition, patentee subjects such bituminous raw material, in an atmosphere of neutral gases, to a temperature only sufficient to render these hydrocarbons fluid, and then to suction by a strong, mechanically produced current of these neutral gases, whereby the hydrocarbons, having been rendered sufficiently fluid by the heating, are separated and removed from the solid constituents of the material treated. The suction, created by the current, materially reduces the pressure in the chamber, where the bituminous raw material is thus treated, thus creating a condition favorable to expansion and assists also materially in extracting the hydrocarbons of higher degree of consistency from among the fibers and pores of its carbon structure.

The neutral gases, enveloping the hydrocarbons thus extracted, constantly, during this transitory period, while they are in this heated and fluid state, prevent their oxidation, and neutralize their tendency to split and form other chemical compounds. Finally, the hydrocarbons are separated from the protecting



neutral gases by condensation. This is effected by cooling the current of neutral gases, conveying the hydrocarbons in their fluid state, though a large proportion of the specifically heavier hydrocarbons is quite rapidly precipitated from the gaseous vehicle as soon as the velocity of the current is diminished. The chemical composition of hydrocarbon constituents of cannel-coal and of similar bituminous materials thus recovered is not changed, or in any respect materially modified. They are recovered in their crude state, and to render them available for further industrial uses, they must be separated from each other and refined. The processes for separating and for refining them are no part of the invention set forth and claimed herein, and therefore are not described.

An apparatus suitable for carrying on this education process is shown illustrating a vertical transverse section thereof, and consists, essentially, of an education chamber, B, designed to be hermetically closed after the charge of the cannel-coal or of a similar bituminous material was placed therein; an exhaustor, F, connected by a conduit, 14, with the bottom part, E,

of the education chamber; chambers 1 for producing or heating the neutral (deoxidized) gases; flues L for conveying these neutral gases into the education chamber; and devices (valves 26) for governing their admission.

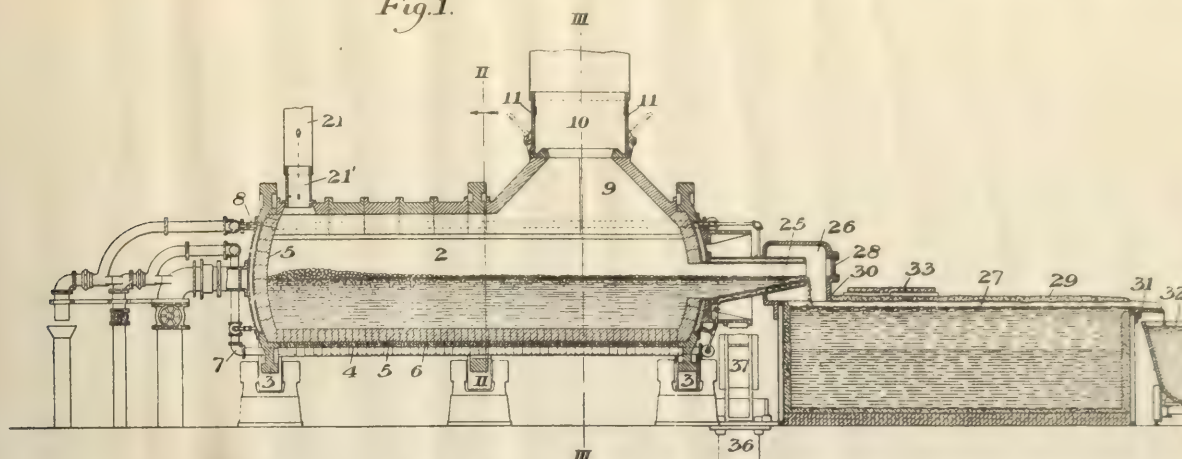
977,996. Method of Smelting and Refining Copper Ores and Compounds. RALPH BAGGLEY, Pittsburg, Pa.

This is a method of extracting copper, gold, silver and other metals from ores, which consists in dissolving or melting ores that contain within themselves oxidizable elements, by sub-

978,211. Art of Extracting Metals Electrolytically. JAMES HART ROBERTSON, New York, N. Y.

This invention is directed to a novel method of extracting gold and other precious metals from their ores after they have been reduced in a very minute or finely powdered state, and it has for its objects, first, to provide a method of effecting this result in as simple, efficient and inexpensive a manner as possible; second, to devise a method of extracting gold when found in other than a metallic state (chlorids, for instance) by the agency of electrolysis and in such manner that the gold

Fig. 1.

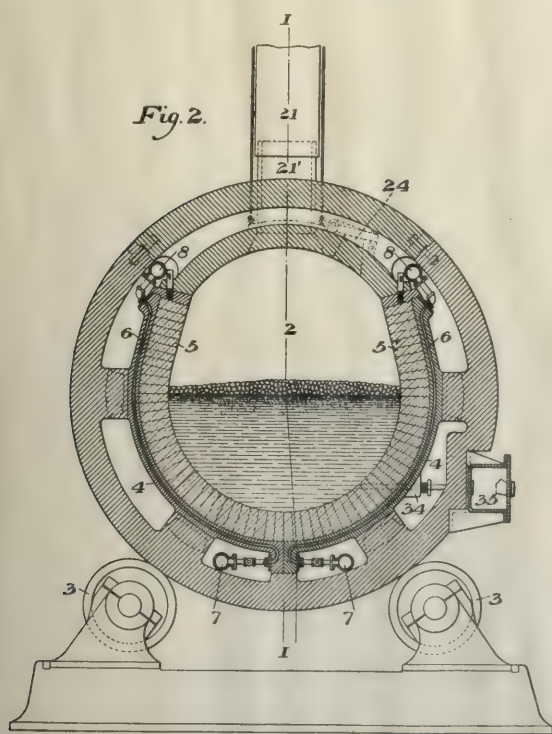


mergence in a molten bath of matte and by the heat of oxidation produced by forcing air through the same, and eliminating the silica, alumina and lime, then separating the slag from the low-grade matte, then transferring the matte into a converter, oxidizing it therein, adding value-bearing silicious ore, and form-

is deposited on the cathode of the apparatus used in practicing said method.

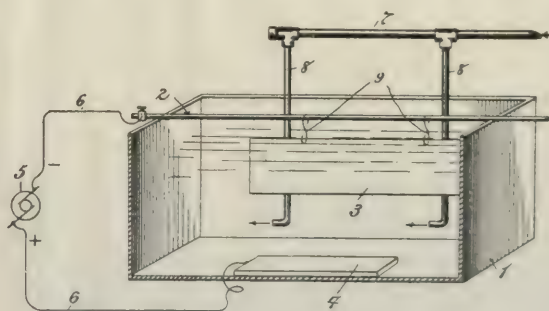
The electrolyte which is illustrated as submerging the anode and cathode when used in the process of extracting gold may be cyanid of potassium or of any other such equivalent materials as are used in the art of electrolytic methods of extracting valuable metals and the anode and cathode may be located in the body of the electrolyte in any preferred manner, or may be of any preferred material and construction or shape, such matters coming well within the skill of those versed in the electrolytic art generally, the essential feature being that they shall be so located as to readily remove the cathode for the

Fig. 2.



ing thereby silicate of iron slags, and then eliminating residual oxidizable impurities by forcing air into the bath.

The accompanying illustration shows apparatus in which the patentees method can be carried out.



purpose of extracting the gold therefrom by fusion in the usual way.

The cathode is illustrated in the drawing as being suspended from the conducting rod 2 by good conducting metallic hooks, 9, 9.

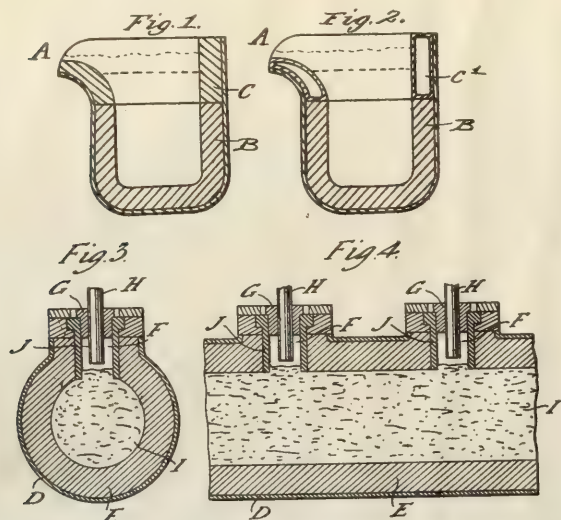
The ore to be treated is first pulverized or ground to a fine powder and gradually fed into the electrolyte which is kept in an agitated condition or circulation by steam, hot air or gas issuing from the sources of supply, not shown, through the pipes 7 and 8. A relatively large amount of the powdered ore will remain in suspension while the liquid is in motion when it is placed in the vat and is simultaneously subjected to the action

of electricity, motion and heat until the major part of the metal is deposited on the cathode 3.

979,337. Manufacture of Steel. ALLEYNE REYNOLDS, London, England.

This invention has for its object the economical production of steel ingots or castings of any desired analysis free from flaws. The patentee first produces a nearly pure iron free from foreign substances, and afterward, just previous to casting, alloy it with certain materials. For the overcoming of the oxidation unavoidable during casting, the extent of which may be ascertained by experience, there is always added the necessary amount of highly exothermic acid and basic-flue-forming additions, in general silicon and manganese.

The process consists in producing a melted charge of iron containing iron oxid in a furnace, teeming and freeing the charge of slag, refining by reduction the slagless charge in a

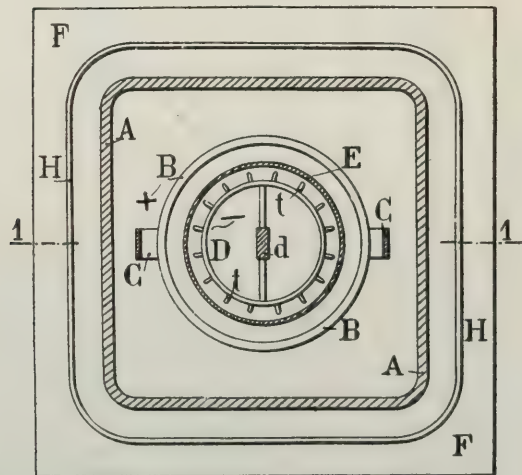


second furnace teeming the refined charge and adding thereto melted alloys and a suitable flux heated in separate furnaces, and casting the charge into a mold.

979,497. Means for the Electrolytic Manufacture of Sodium. PAUL LEON HULIN, Grenoble, France.

In order to set the apparatus in action the vessel A is filled with caustic soda in fragments and the electric current is caused

Fig.1

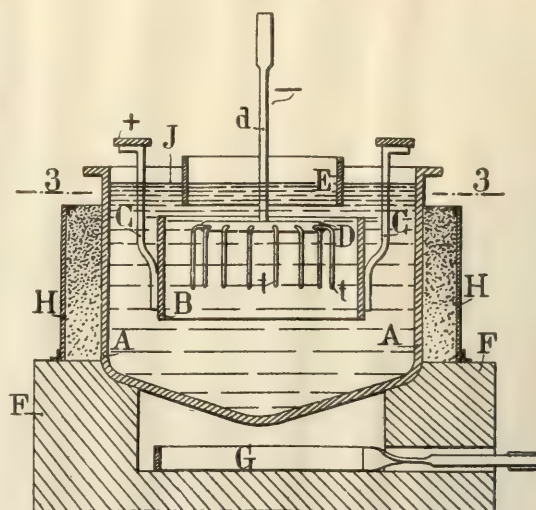


to traverse the conductor G; the intensity of the current is regulated so as to bring the conductor to red-heat. The heat

disengaged is absorbed by the metal of the vat, and the soda which it contains becomes fused. As soon as the vessel is full of liquefied soda the current is stopped flowing in the heating circuit G and the apparatus is ready for work.

The production of sodium is initiated by passing a continuous

Fig.2.



current, whose intensity is proportioned to the dimensions of the apparatus and under a pressure of about 5 or 6 volts, the resistance which the current experiences in traversing the bath causing the development of sufficient heat to maintain

Fig.3.

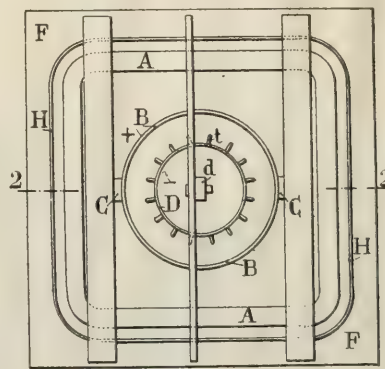


Fig.4.

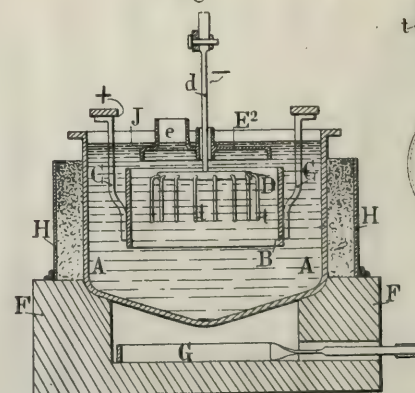


Fig.6.

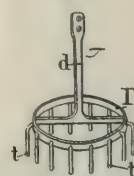
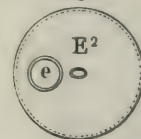


Fig.7.



the soda in the fused state. Under the electrolytic action of the current free oxygen is formed at the anode and is disengaged at the surface externally of the separator E, while the hydrogen

and sodium simultaneously escape from the cathode in globules and both appear at the surface of the bath in the interior of the ring E. The sodium collects in drops resembling melted white wax, and it is removed by means of a perforated ladle which only permits the passage of the fused soda.

The apparatus is charged periodically with soda to replace that which has been decomposed. The mean level of the bath is indicated at J.

The accompanying illustration shows the patentees apparatus.

979,663. Electric Furnace. BAYARD GUTHRIE, Pittsburgh, Pa., AND JOSEPH P. KARCH, Plainville, Connecticut.

In the operation of this furnace the crucible 1 is charged, the car placed on top and the electrodes 2, 3, 4 and 5 are all moved up into contact with the crucible. Current is then turned on and the crucible and its contents are in the circuits. This warms up the crucible and contents but as the electrodes are purposely made large and as the crucible and contents are relatively good conductors the heat is not great. The handle 40 is then applied to the end of one of the screws, 38, and the electrodes are slowly withdrawn from contact with the crucible. Arcs immediately form between the pair of electrodes 2 and 3 and the pair 4 and 5 with the crucible in the center of intense heat.

The great heat soon melts the contents of the crucible. The

When it is particularly desired to avoid oxidation of the contents of the crucible a neutral or inert gas may be supplied through the pipe 19 and which will pass through the perforated stand 18, up around the crucible 1, and out through the opening in the top of the casing surrounding the crucible mouth. This will prevent the air from reaching the contents of the crucible. Similarly a combustible gas may be supplied and burned as it escapes from the opening in the top of the casing. This will have a tendency to withdraw oxygen from the contents of the crucible and thus act as a reduction agent.

INDUSTRIAL AND TRADE NOTES.

ADVANCE CHAPTER FROM MINERAL RESOURCES OF THE UNITED STATES.

LITHIUM IN 1909.

Lithium is one of the alkali metals and is the lightest known solid element. Its specific gravity (0.585) is so low that it will float on kerosene. Although traces of lithium are found in nearly all igneous rocks¹ and in many springs, and notable quantities of several lithium minerals occur in the United States at widely separated points, such minerals are not at all common.

In all places where lithium minerals visibly occur they are associated with granitic rocks and generally, if not always, with the latest phases of granitic intrusions, either in pegmatites or in granites and adjacent rocks which have been altered by hot gaseous emanations—a process known as pneumatolysis or pneumatolytic action. In some places large masses of lithium minerals which can be worked commercially are found in pegmatites, but in the altered granites only minor quantities of lithia mica are found. The places of occurrence of lithium are practically those of tin, but the large deposits of tin seldom contain workable deposits of lithium minerals. In the pegmatites, which may carry large quantities of lithium minerals, the tin deposits are generally small.

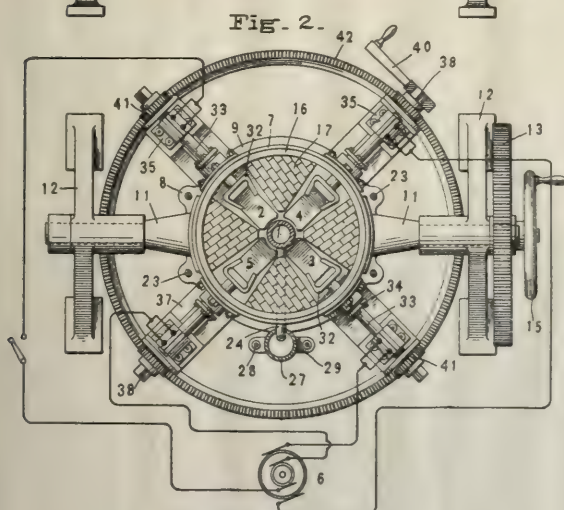
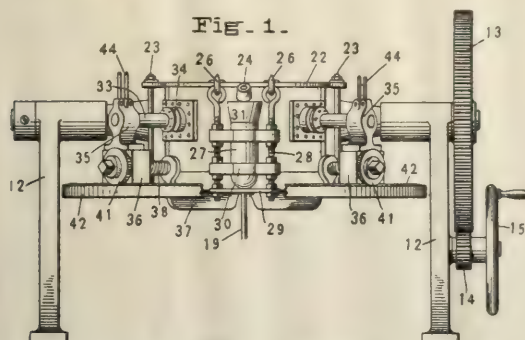
Lepidolite.—Lepidolite ranges in color through glistening white, yellowish, violet and lilac tints. It occurs generally in small indistinct plates but in places forms six-sided crystals belonging to the monoclinic system. At Pala, Cal., and at other places it forms an outer rim around muscovite plates several inches across.

In the United States lepidolite is found in Hebron, Auburn, Norway, Paris, Rumford, and other places in western Maine; in South Dakota in considerable quantities in connection with the tin deposits of the southern Black Hills; and in great quantity with the beautiful red tourmaline, rubellite, in the neighborhood of Pala, San Diego County, Cal. At the Stewart mine, 2 miles north of Pala,² a mass of delicately tinted lilac-colored lepidolite showed a lenticular surface exposure 90 feet broad and 25 feet thick. In 1907 a drift at right angles to the exposure had been driven 125 feet in the lepidolite. Several hundred tons were mined and shipped from this deposit. Rubellite, also containing lithia, forms beautiful radial aggregates enclosed in the mass of lepidolite. Many thousand specimens obtained from this locality are distributed through the mineral collections of the world. After the spodumene and amblygonite deposits in the Black Hills of South Dakota were opened up it no longer paid to operate the Pala deposits. In the Black Hills lepidolite also was at one time worked to a small extent for its lithia content. At many other localities lepidolite is found in occasional flakes or small masses. At Wakefield, Canada, lepidolite occurs in plates several inches across.

Other lithium micas are cookeite, zinnwaldite, cryophyllite, polyolithionite, and protolithionite. Zinnwaldite containing

¹ Clarke, F. W., "The Data of Geochemistry," *Bull. U. S. Geol. Survey*, **330**, 17 (1908).

² Personal communication from W. T. Schaller, U. S. Geol. Survey.



electrodes are then closed into contact with the crucible, the arcs gradually decrease and the current is turned off. The mold 27 being hung on the hooks 26, 26, the hand wheel 15 is rotated so as to tilt the furnace and pour the contents of the crucible into the mold. The electrodes hold the crucible while pouring. When one mold is filled it can be quickly removed and another substituted and pouring continued until the crucible is empty. The furnace is then returned to its horizontal position and the operation repeated.

3.36 per cent. lithia was formerly worked at Zinnwald, Germany, for its lithium content.¹

Triphylite occurs in small amounts at Peru, Me.;² Norwich, Mass.;² Grafton, N. H.;² and lithiophilite at Branchfield, Conn.,² and Tubb's farm, Me.² Minerals which probably belong to this group, but which are badly weathered or of which no analyses are known, occur in the tin-bearing pegmatite dikes of Kings Mountain, N. C., near Pala,³ and in the Black Hills. In the Black Hills such a mineral occurs in many pegmatite dikes, probably in all which carry either lepidolite, spodumene, or amblygonite. The masses are very irregular in size and shape and are of a brownish or blackish color, in the latter case probably owing to the oxidation of some of the manganese. In places, both in South Dakota and in North Carolina, surfaces are coated with a fine purple film of purpurite, a decomposition product. In the Etta mine, South Dakota, masses of the mineral 3 to 4 inches in diameter have decomposed, leaving cavities partly filled with lilac, blue, and dark green vivianite, probably accompanied by another iron phosphate, dufrenite. In both the Etta and the Peerless mines a lithiophilite-like mineral occurs in sufficient abundance to yield a few tons annually in the course of mining for other minerals. As stated it contains from 8.15 to 9.36 per cent. of lithia, and if it occurred in large quantity would be equal to amblygonite as a lithia ore.

Probably both triphylite and lithiophilite occur in the Black Hills.

Alluaudite is a mineral closely related to lithiophilite, but of no commercial value.

Spodumene.—Spodumene occurs in the same general localities mentioned for lepidolite, but is found in greatest quantity in the Black Hills. In the Etta mine, $1\frac{1}{2}$ miles south of Keystone, the crystals of spodumene are immense, and so far as known are approached in size by no crystals found outside of the Black Hills. One crystal was 42 feet in length, with a cross section of approximately 3 by 6 feet. Part was decayed and useless, but about 37 tons of spodumene were mined from it.⁴ At many places mining has exposed cross-sections which are rectangles with truncated corners. Spodumene occurs—as do each of the other minerals mentioned—in pegmatite dikes. The dike at the Etta mine is oval in shape and about 150 by 200 feet in horizontal measurement. Tin was first discovered in the Black Hills in this mine, and previous to that the mine had been worked for mica. The crystals are considerably decayed, have an earthy appearance and the odor of a fresh clay pipe. Owing to the decay, the crystals have a fibrous, woody structure, and from this and their size the workmen ordinarily refer to them as “logs,” which they much resemble. Cassiterite has been deposited along cracks in the spodumene and is evidently of later crystallization. It is an odd fact that amblygonite is almost wholly absent from this deposit, though in the Peerless claim half a mile away it occurs in large masses, with some spodumene.

Spodumene of an emerald-green color, when fresh enough to be glassy and clear, is known as hiddenite and sells for very high prices as a gem. As with most gems, the price is largely artificial. It is found at Hiddenite, N. C. A beautiful pink or lilac variety found near Pala and Rincon, San Diego County, Cal., is known as kunzite, and also sells at high prices. Some jewelers say that the stones lose their color, probably from strong light, and one jeweler showed the writer a stone which he said had faded in a comparatively short time. Kunzite when of a good clear color is one of the most beautiful of gem stones. In hiddenite and kunzite the refraction of light is high, so

that the stones have considerable brilliancy. Both varieties are reported from Madagascar.¹

Beta-spodumene, cymatolite, and killinite are alteration minerals formed from spodumene, which have only mineralogical importance.

Petalite, castorite, and hydrocastorite are lithium minerals related to spodumene, but are without commercial value as a source of lithia.

Amblygonite.—Amblygonite is found in the same general localities that have been noted for lepidolite and spodumene. It contains a larger percentage of lithia than any mineral except lithiophilite, and, as it occurs in masses large enough to be easily and cheaply worked, it is more valuable, other conditions being equal, as a source of lithia than either of the other minerals. As found in South Dakota and California, it is a pearly white mineral with one good cleavage, and looks like a very fresh feldspar. In other places it has pale greenish, bluish, yellowish, or brownish tints. In 1907 and 1908 Mr. Herman Reinbold, of the Western Chemical Reduction Company, Omaha, Nebr., mined a large deposit of amblygonite of excellent quality on the Peerless claim, half a mile northeast of the Etta claim and 1 mile from Keystone, S. Dak. The shoot or mass of amblygonite was about 20 feet wide and had been excavated more than 20 feet in depth and 20 feet in length. This mass is said to have produced a total of 900 tons.

After the mining of amblygonite began on the Peerless claim at Keystone, S. Dak., the price of lithium carbonate fell from \$2 or \$2.50 per pound to 50 cents per pound, and large quantities have been sold at still lower prices.

The market for lithium minerals and salts has been a restricted one, as few uses have been known and the number of large consumers has been small. The product most manufactured is lithium carbonate, and for some time it was not widely known what use was made of the bulk of the product. Its use in the manufacture of artificial lithia waters and for medicinal purposes would account for only a few hundred pounds a year. It is now becoming generally known that it is mainly used in the manufacture of storage batteries. A small quantity probably also goes into the manufacture of fire-works.

Lithium (the metal) has no known practical use. It oxidizes very readily, is soft, not very tenacious, and is not known to have other properties that might make it economically valuable.

Of the lithium salts, lithium bromide is used in photography and in medicine, and various other salts are used for lithiasis (gravel), arthritis (inflammation of the joints), chronic rheumatism, and gout.

By many the use of natural lithium-bearing waters for various diseases is highly valued, especially in lithiasis, and a large trade is carried on in water from “lithia springs” in many parts of the United States. Concerning the medicinal use of lithium-bearing spring waters, Haywood and Smith² remark:

While lithium seldom or never occurs in waters in large enough quantities to be a predominating basic constituent, still it does often appear in sufficient quantities to have a decided therapeutic action. These compounds are active diuretics and form a very soluble urate which is easily eliminated from the system. Waters of the above class therefore find their greatest application in the treatment of rheumatism, rheumatic tendencies, and gout. In cases of gravel and calculi they are also valuable disintegrating agents.

The same authors found that among the various lithia waters, that from the Carlsbad Spring of Saratoga carried the largest proportion of lithium, namely, 31.8 parts of lithium chloride

¹ Singewald, Jos. T., Jr., “The Erzgebirge Tin Deposits,” *Econ. Geol.*, 5, 173 (1910).

² Dana, *op. cit.*

³ Personal communication from W. T. Schaller.

⁴ Personal communication from A. M. Lane, Keystone, S. Dak.

¹ Sterrett, Douglas B., “Mineral Resources of U. S. for 1907,” *U. S. Geol. Survey*, 2, 826 (1908).

² Haywood, J. K., and Smith, B. H., “Mineral Waters of the United States,” *U. S. Dept. Agr., Bureau of Chemistry, Bull.* 12 (1905).

per million. Some of the so-called lithia waters contain only extremely small quantities of lithia.

In 1909 several carloads of amblygonite were shipped by the Western Reduction Company, of Omaha, Nebr., from its property near Keystone, S. Dak., and a few carloads of spodumene were shipped from the Etta claim by the Standard Essence Company to its works at Maywood, N. J. In view of the limited number of producers exact figures of production are not published.

TUNGSTEN IN 1909.

With the recovery of the steel trade during 1909 prices for tungsten rose above those of 1908, and mining quickly responded. The mines in Colorado (Boulder County) and in California turned out quantities of ore comparable with those of 1907, and properties were developed at Deer Trail, Stevens County, Wash., and at Osceola, Nev., which promised a considerable effect in the near future upon the tungsten trade of the United States. Interest in and knowledge of tungsten minerals have become so wide-spread that prospectors generally are on the lookout for them, and new occurrences are reported from time to time.

Owing to errors in several returns of tungsten ore produced during the year 1909, the preliminary figures published in January, 1910, were too high. The figures as corrected by later returns indicate a production of 1,619 tons of 60 per cent. ore, valued at \$614,370. The production of tungsten ores in the United States from 1900 to 1909, inclusive, has been as follows:

PRODUCTION OF CONCENTRATED TUNGSTEN ORES IN THE UNITED STATES, 1900-1909, IN SHORT TONS.¹

Years.	Quantity.	Value.
1900.....	46	\$11,040
1901.....	179	27,720
1902.....	184	34,040
1903.....	292	43,639
1904.....	740	184,000
1905.....	803	268,676
1906.....	928	348,867
1907.....	1,640	890,048
1908.....	671	229,955
1909.....	1,619	614,370

The price of tungsten ores ranged from \$5 to \$9 per unit, depending upon quantity, quality, and the immediate need of the buyer. The average price was between \$6 and \$6.50 per unit.

Although the figures from all the countries producing large quantities of tungsten ores are not yet available, enough are at hand to show that the world's production for 1909 was larger than that for 1908, and was possibly equal to that of 1907. In very few of the returns, however, is the percentage of tungsten trioxide indicated and this is a prime necessity in comparing figures. It is probable that most of the exported ore is richer than 60 per cent. in tungsten trioxide, and that the figures are therefore low.

THE WORLD'S PRODUCTION OF TUNGSTEN ORE, 1905-1909, BY COUNTRIES, ESTIMATED AS FAR AS POSSIBLE IN SHORT TONS OF CONCENTRATES CONTAINING 60 PER CENT. OF TUNGSTEN TRIOXIDE.

Country.	1905.	1906.	1907.	1908.	1909.
Africa: South Africa.....	9	211	40	16 ²	
Asia:					
Federated Malay States	151	89	83 ³	99 ³	
Siam.....		10			

¹ The production of tungsten ores in this country from year to year can be fairly compared in this table only since and beginning with 1906, as before that date no effort had been made to reduce the ores to a common basis of concentration. Since 1906 the ores have been, as far as possible, reduced to an equivalent of ore carrying 60 per cent. tungsten trioxide (WO₃), which is the ordinary commercial basis in the United States.

² Fourth annual statement of the trade and shipping of the colonies and territories forming the South African Customs Union, 1909, Cape Town, 1910, Table 44. The percentage of tungsten trioxide in the ores is unknown.

³ *Min. Jour.*, London, 91, October 8, 1910, p. 1174. Exports for 1908 and 1909.

Country.	1905.	1906.	1907.	1908.	1909.
India.....					7 ¹
Australia:					
New South Wales.....	251	270	351	269	434 ²
South Australia and Northern Territory.....	1	230	27	40	49 ³
Queensland.....	1,082	865	753	116	67 ³
Tasmania.....	36	22	46	5	20
Victoria.....				3	3
Western Australia.....					6 ²
East Indies:					
Billiton.....			4	1	
Singkep.....			1	14	23 ⁵
Europe:					
Austria.....	65	63	50	44	43 ⁶
England.....	193	304	361	261	421 ⁶
France.....	28	20	67	124	
German Empire.....	42	87	68	46	106 ⁷
Italy.....	36	28	18		
Portugal.....	320	629	702	684	609 ²
Spain.....	413	222	303	249	
Oceania: New Zealand.....	64	121	153	87	78 ⁴
North America: United States.	803	928	1,640	671	1,619
South America:					
Argentina.....		326	507	548	909 ⁸
Bolivia.....	75	75	500	187	168 ⁹
Brazil.....				16	
Total.....	3,979	4,320	6,062	3,898	5,289

NICKEL AND COBALT IN 1909.

The only metallic nickel and the only cobalt known to have been produced in the United States from ores mined in this country during 1909 came from Fredericktown, Mo., where the North American Lead Company operated a smelter for the extraction of nickel, cobalt and copper from sulphides accompanying galena. Both nickel and cobalt were produced in this country from Ontario ores during the year.

In refining copper by the electrolytic process, the electrolyte generally soon shows nickel sulphate in solution, and must be watched in order that more than 1 per cent. of the sulphate be not allowed to accumulate, as more than 1 per cent. is said to affect injuriously the deposition of the copper on the cathodes. Nickel is carried in minute quantities by crude copper from many places, but which ores produce it can not ordinarily be told, as the refineries which report a nickel saving refine pig copper from many localities and from several countries. In 1909 the United States Metals Refining Company at its Chrome, N. J., plant, the Nichols Copper Company at its Laurel Hill, Long Island refinery, and the Orford Copper Company at its refineries at Constable Hook, N. Y., and Bayonne, N. J., made large quantities of nickel sulphate and nickel ammonium sulphate. The total quantity of the two salts produced during 1909 was 3,101,505 pounds valued at approximately \$62,000. It is

¹ *Min. Jour.*, London, 91, October 22, 1910, p. 1222.

² *Ann. Rept. Dept. Mines*, New South Wales, for 1909, Sydney, 1910, pp. 58-59. The figures given represent exports of 193.3 long tons of scheelite and 127 long tons of wolframite, a total of 320.3 long tons. Concerning scheelite the report states: "The prices realized locally ranged from £65 (\$316) to £130 (\$632) per ton for 72 per cent. ore." The tungsten ore has therefore been considered to carry 72 per cent. WO₃.

³ *Min. Jour.*, London, 88, February 26, 1910, p. 237.

⁴ *Queensland Govt. Min. Jour.*, Brisbane, March 15, 1910, p. 122.

⁵ *Progress Min. Ind. Tasmania*, Hobart, 1909 and 1910 (quarterly).

⁶ *Ann. Rept. Sec. Mines for 1909*, Melbourne, 1910, p. 25.

⁷ *Min. Jour.*, London, 91, November 19, 1910, p. 1320.

⁸ Fiscal year June 30, 1908, to June 30, 1909. *Min. Jour.*, London.

⁹ *Min. Jour.*, London, 91, November 12, 1910, p. 1306.

¹⁰ *Mines and Quarries*, Gen Rept. with Statistics for 1909, Home Office, London, 1910, p. 10.

¹¹ WO₃, *Min. Jour.*, London, 91, December 10, 1910, p. 1409. Output of Saxony.

¹² *Boletim commercial e maritimo*, Dezembro, 1909, Lisbon, 1910, p. 791.

¹³ Papers and reports relating to minerals and mining, Wellington, 1910, p. 17. The exports of scheelite for the year were 58 long tons thought to carry 72 per cent.

¹⁴ *El Comercio Exterior Argentina*, Buenos Aires, 1910, p. 191.

¹⁵ Communicated by Bureau American Republics, September 26, 1910.

difficult to estimate how much of the entire quantity should be credited as the production of the United States, possibly a third. The distribution of this quantity among the different States would be impossible.

At Webster, N. C., the North Carolina Nickel Company spent a large amount of money putting in a plant for the electrical reduction of low-grade silicate ores. It is the intention to make a ferronickel-silicon, and thus avoid complicated metallurgical processes. The ferronickel-silicon is to be sold for steel-making. The present steam plant and electrical machinery are reported to have cost \$600,000. The company plans to utilize also a water power near at hand. Diamond drilling and trenches are said to show a sufficient supply of nickel ore on hand.

The imports for consumption of nickel into the United States since 1902, inclusive, as reported by the Bureau of Statistics, have been as follows:

IMPORTS OF NICKEL FOR CONSUMPTION INTO THE UNITED STATES, 1902-1909.

	Nickel, nickel ore, and matte, nickel oxide, alloys of nickel with copper, etc.		Value of manufactured articles of nickel.	Total value.
	Pounds.	Value.		
1902.....	33,942,710	\$1,407,521	\$30,128	\$1,437,649
1903.....	36,217,985	1,456,605	37,284	1,493,889
1904.....	19,739,315	1,118,541	2,950	1,121,491
1905.....	31,072,206	1,958,840	3,291	1,962,131
1906.....	34,082,042	1,867,568	8,963	1,876,531
1907.....	18,598,638	2,233,867	9,159	2,243,026
1908.....	16,825,291	2,487,605	9,980	2,497,585
1909.....	22,194,102	3,034,407	1,866	3,036,273

The imports for 1909 were divided as follows:

IMPORTS OF NICKEL FOR CONSUMPTION INTO THE UNITED STATES IN 1909.

	Pounds.	Value.
Oxides.....	25,798	\$9,235
Nickel, alloys, pigs, bars, etc.....	252,113	94,784
Ore and matte (nickel content).....	21,916,191	2,927,975
Sheets or strips.....	2,413
Total.....	22,194,102	3,034,407

The imports for consumption of cobalt into the United States since 1901 have been as follows:

COBALT OXIDE, ORE, AND ZAFFER IMPORTED INTO THE UNITED STATES FOR CONSUMPTION, 1901-1909, IN POUNDS.

Years.	Quantity.	Value.
1901.....	71,969	134,208
1902.....	79,984	151,115
1903.....	73,350	145,264
1904.....	42,354	86,925
1905.....	70,048	139,377
1906.....	41,084	83,167
1907.....	48,013	74,849
1908.....	219,098	17,077
1909.....	12,132	11,696

EXPORTS.

The United States refines much more nickel than it can use, so that although not an important producer it is a large exporter. Exports since 1901 have been as follows:

EXPORTS OF NICKEL, NICKEL OXIDE, AND MATTE FROM THE UNITED STATES, 1901-1909, IN POUNDS.

Year.	Quantity.	Value.
1901.....	5,869,655	\$1,521,291
1902.....	3,228,607	924,579
1903.....	2,414,499	703,550
1904.....	7,519,206	2,130,933
1905.....	9,550,918	2,894,700
1906.....	10,620,410	3,493,643
1907.....	8,772,578	2,845,663
1908.....	9,770,248	3,297,988
1909.....	12,048,737	4,101,976

VANADIUM IN 1909.

The larger part of the vanadium used in this country is obtained from ore imported from Cerro de Pasco, Peru, by the

American Vanadium Company, of Pittsburg, Pa. The ore is largely patronite, a sulphide of vanadium, with which are various oxides in the weathered part of the deposit.

In this country vanadium was produced in 1909 by the Vanadium All ys Company, at Newmire, Colo., from the roscoelite-bearing sandstone at that place. Much trouble has been experienced with the melting down of the furnaces in which the ore is given a chloridizing roast, and the percentage of recovery has not been all that could be wished. About the last of the year the plant passed into the hands of the Primos Chemical Company.

The Colorado Vanadium Company established a laboratory at Boulder and pursued experiments on the extraction of vanadium from the Newmire roscoelite, but produced no ore beyond a small quantity needed in its experimental work.

The General Vanadium Company shipped two cars of vanadiferous sandstone from the Jodandy claim in the Paradox Valley, 58 miles northwest of Placerville, Colo. Most of the vanadium in this sandstone is in a black mineral, probably an oxide, but not thoroughly investigated.

In New Mexico occurrences of vanadium minerals are said to have been prospected near Hillsboro and in the Caballos Range, but no production is known to have been made.

So many letters asking for tests for vanadium are received by the United States Geological Survey that the following tests, which have been found effective, are given:

To test for vanadium, the mineral may be digested, with nitric acid. If hydrogen peroxide be added to the resulting liquid, a brown color will appear if vanadium is present.

Some vanadium minerals are also attacked by hydrochloric acid and by sulphuric acid. To the solution resulting from the use of either acid, hydrogen peroxide may be added, and a brown solution will show the presence of vanadium, as when nitric acid is used. If either hydrochloric or sulphuric acid is used, metallic zinc may be added after hydrogen peroxide, and a bright blue color will be given by the reduction of vanadium compounds. The same effect can be obtained in a nitric acid solution by adding sulphuric acid, evaporating to white fumes, diluting, and adding metallic zinc. If preferred, hydrochloric acid instead of sulphuric acid may be added to the nitric acid solution, but in that case evaporation must be carried almost to dryness at least twice to get rid of the nitric acid. The liquid may then be diluted and more acid added, followed by zinc as described.

At times the tests given above are not wholly satisfactory. In such cases, if the apparatus is at hand, through a filtered solution made alkaline with ammonia pass hydrogen sulphide (H_2S) gas until the solution is saturated. The solution will take a fine garnet or deep wine color if vanadium is present. Copper, if present, is precipitated as a sulphide and does not interfere with the test.

If commercial iron sulphide for making hydrogen sulphide gas is not at hand, iron pyrites, galena, or zinc blende may be used with hydrochloric acid. The only accessories needed are two test tubes, one of which is closed with a cork in which is inserted a bent tube, the other end of which can be placed in the solution to be tested for vanadium.

TITANIUM IN 1909.

During 1909 rutile (titanium oxide) was mined at two places in Nelson County, Va. The General Electric Company did a large amount of prospecting upon the Warwick farm, 7 miles northwest of Tye River postoffice during the winter, spring and summer, and later leased the American Rutile Company's mill and quarry at Roseland, about 4 miles farther northwest.

The rutile deposits on the Warwick farm were found to be so discontinuous that work was given up after more than a year's prospecting. About 100 tons of rutile ore, carrying

50 per cent. TiO_2 , were shipped to a Pennsylvania company for concentration, and are reported to have yielded 35 tons of concentrates.

Eighty-six tons of concentrates, carrying between 80 and 90 per cent. TiO_2 , were produced at the Roseland mill.

The concentrates from both places were further treated by a magnetic separator. The total value of the concentrates from both places is estimated at \$10,000.

A carload of nelsonite, composed of ilmenite and apatite, was shipped from a dike near Roseland by the General Electric Company for experimental work.

The Titanium Alloy Manufacturing Company, of Buffalo, uses both rutile and ilmenite in making ferrotitanium. The company states that the ilmenite it uses comes from Canada.

No rutile is known to have been imported into the United States in 1909, but the American Rutile Company was an exporter of rutile concentrates. So far as is at present known its deposits at Roseland are the largest in the world.

The use of titanium in making steel rails increased considerably during the year. The New York Central lines have given rails treated with ferrotitanium a long trial, and concerning these rails W. C. Brown, the president of the system, makes the following statement in a published letter:

Under the heaviest traffic we have ever had these rails are giving perfect satisfaction.

We have subjected them to the most exacting service at the throat of the Grand Central terminal yard; and under traffic which made it necessary to change other rails within six or eight months, the ferrotitanium rails, which have been in service a year, show almost no appreciable wear.

In this connection I would say that the Bessemer rails rolled by the Lackawanna Steel Company for our lines for the past two years (all of which have been treated with titanium) have been the best we have ever received, and in many respects we regard them as equal, if not superior, to the average open-hearth steel. While the quality is so much better the cost is insignificant, and we are now specifying titanium alloys in all of our rails.

The use of titanium in arc-light electrodes is also growing. Of these there are two principal types, one of which is an electrode made of finely ground titanium carbide, the other is composed of magnetite, chromium oxide and rutile.

MOLYBDENUM, URANIUM AND TANTALUM IN 1909.

No production of molybdenum or uranium minerals and only a small output of a tantalum mineral is known to have been made in the United States during 1909. The demand is not large for either the metals or their salts.

The use of molybdenum in steel has not grown greatly, and no molybdenum deposits have yet been developed in this country to a point where they could be depended upon for any considerable production.

Up to the close of the year no one had established a method by which the low-grade carnotite deposits of Colorado could be profitably worked, though there are apparently large quantities of rock carrying from 1 to 2 per cent. of uranium oxide (U_3O_8), while smaller lots containing as high as 8 or 9 per cent. may be mined.

Tantalum incandescent electric lamps have such strong competition in tungsten incandescent lamps that the demand for tantalum minerals seems rather to have decreased than grown. A small tonnage of columbite (a tantalate and columbate of iron and manganese) was mined in 1909 by the Western Reduction Company, of Omaha, Nebr., from a claim near Keystone, S. Dak., which it was operating for amblygonite. The tantalum used in this country in 1909 was imported from Germany.

TIN IN 1909.

Tin remains one of the few commercial metals of which the United States is not an important producer, although this country is the largest consumer of the metal, taking about 43 per cent. of the world's production.

Alaska.—On Cape Mountain, 5 miles southeast of Cape Prince of Wales, the Bartels Tin Mining Company continued prospecting work and reported having a considerable quantity of ore on their dumps. The company has been prospecting at this point since 1903. A 10-stamp mill with concentrating tables was erected in 1905, and the following year about 10 tons of concentrates were produced. Since then there has been no production.

Southwest of the Bartels Tin Mining Company's mine and near the top of Cape Mountain, the United States-Alaska Tin Mining Company has been working since 1903 or 1904. Since 1905 it has been driving a crosscut tunnel to cut a vein exposed near the top of Cape Mountain.

Only one company, the American Mining Company, operated on Buck Creek during 1909. Seventeen short tons of stream tin, carrying between 67 and 68 per cent. tin, equivalent to 19 tons of 60 per cent. ore, were taken out in the course of assessment and prospecting work. The ore was shipped to Penzance, England, and was sold for $33\frac{1}{3}$ cents per pound of metallic tin contained, a total of about \$12,667. Prospecting is said to have shown that the tin extends farther into the tundra on both sides of Buck Creek than had been supposed, and the installation of a dredge is contemplated. The season of 1909 was short, cold, and stormy, and only assessment work was done on other claims along the creek.

Some prospecting for tin was done on Ears Mountain, Brooks Mountain, and Lost River.

South Dakota.—The Pahasa Mining Company took over in 1909 the properties of the old Harney Peak Tin Mining and Manufacturing Company near Hill City, which had been in the hands of the court for fourteen or fifteen years. Dumps were sampled, workings were examined, and shafts were unwatered and cleaned with a view to ascertaining the real value of the deposits.

The Gertie Mining and Milling Company continued work upon its mill just south of Hill City.

At Tinton, the Tinton Reduction Company has done further work both on the mill and in the mine, and 24 short tons of tin concentrates were shipped in 1909 to Chicago and smelted, giving a return of \$4,832. The pegmatite in which the ore occurs is crushed dry and a steady blast of air is driven against a falling stream of the finely crushed ore, blowing out the flat leaves of mica, which is said to be a merchantable product. The ore is reported to average 0.5 per cent. tin.

Texas.—The tin deposits in the Franklin Mountains, 15 miles north of El Paso, which were owned and prospected by Mr. C. R. Morehead, of El Paso, and later by the Florella Mining Company, passed in 1909 into the hands of a new company, the El Paso Tin Mining and Smelting Company, which continued prospecting and reported having uncovered larger quantities of ore than were before known.

At Streeter, Mason County, P. H. Parker, whose discovery of tin ore was noted in the report for 1908, continued prospecting in 1909, but nothing of commercial value seems to have been developed.

Other States.—No work is known to have been done during 1909 on the deposits in North Carolina, South Carolina, Virginia, or Washington.

The world's supply of tin for the last three years, as shown by shipments and sales, has been approximately as follows:

SUPPLY OF TIN IN 1907, 1908 AND 1909, IN SHORT TONS.

	1907.	1908.	1909.
Total shipments:			
Straits Settlements.....	58,800	67,760	65,459 ¹
Australia.....	7,112	6,552	5,992 ²
Bolivia.....	17,136	19,040	23,523 ³
South Africa.....	...	1,904	916 ⁴
China.....	224
Banka sales in Holland.....	12,197	12,880	12,992 ²
Billiton sales in Java.....	2,408	2,465	2,465 ²
Production in Cornwall.....	5,488	6,048	5,802 ²
Total.....	103,365	116,649	117,149

During the year 1909 the United States imported for consumption 47,662 short tons of metallic tin, valued at \$27,558,546; 1,432 tons of cassiterite, valued at \$68,462; tin foil valued at \$23,427; and other manufactures of tin, valued at \$55,714. The quantity imported has been exceeded but once before, in 1906. The imports of tin for consumption into the United States since 1901 have been as follows:

TIN IMPORTED AND ENTERED FOR CONSUMPTION IN THE UNITED STATES, 1901-1909, IN SHORT TONS.

Years.	Quantity.	Value.
1901.....	37,280	\$19,024,761
1902.....	42,522	21,263,337
1903.....	41,567	22,265,336
1904.....	41,472	22,356,895
1905.....	44,188	26,316,023
1906.....	50,477	37,447,315
1907.....	41,257	32,074,263
1908.....	41,267	23,923,560
1909.....	47,662 ⁵	27,558,546

The average price of tin as indicated by the imports for consumption during 1909 was 28.91 cents per pound. As given by C. Mayer⁶ the average price in New York for the year was 29.69 cents per pound. "Metal statistics, 1910,"⁷ gives the average price as 29.76 cents per pound.

There was a gradual, steady rise in the monthly average of prices from about 28 cents per pound in January to about 29³/₄ cents per pound for December. The lowest price was 27¹/₄ cents in February, and the highest was 34¹/₈ cents, reached in December. Although the average price for the year was very little more than during 1908 (about 29.5 cents), the fluctuations were somewhat greater. During 1908 the lowest price was about 26.5 and the highest about 32.5 cents per pound.

PRODUCTION OF ANTIMONY IN THE UNITED STATES, 1903-1909, IN SHORT TONS.

Years.	Contained in antimonial lead of domestic origin.		Contained in antimonial lead of foreign origin, but smelted in the United States.		Antimony produced from domestic ore.		Recovered from old alloys, scrap, dross, etc.	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
1903.....	2,558	\$445,092	570	\$103,341
1904.....	2,571	443,598	486 ²	61,926
1905.....	2,747	588,354	493	117,433
1906.....	1,362	544,800 ³	404 ⁴	58,149
1907.....	1,561	508,886 ⁵	351 ⁴	77,300
1908.....	2,246	359,360 ⁶	(7)	(8)
1909.....	1,617	252,252 ⁸	743	115,908 ⁷	(7)	(8)	1,556	\$242,736 ⁸

Statistics gathered by John P. Dunlop, of the United States Geological Survey, indicate growth in the recovery of tin from tin scrap, used tin cans, old tin pipe, worn driving-box linings,

¹ Figures quoted from official sources by *Min. Jour.*, London, **88**, 1910, 65 (1910).

² Exports, as given by C. Mayer in "Annual Statistical Report of the New York Metal Exchange for 1909," p. 13.

³ *Min. Jour.*, London, **88**, 336 (1910). Senor Ventura Farfan, inspector of custom houses (Bolivia), is quoted as giving the exports upon which duty was paid as 35,566.4 metric tons of barilla (concentrates) carrying 60 per cent. tin. Although a part was pig tin from Oruro, it was calculated to a basis of 60 per cent. concentrates.

⁴ Fourth annual statement of the trade and shipping of the colonies and territories forming the South African Customs Union, Cape Town, 1910. Tin ore to the amount of 27,255 hundred weight was shipped during 1909. This is considered as giving a recovery of 60 per cent. tin.

⁵ This item does not include the tin contained in imported ore, tin foil, or other manufactures.

⁶ *Op. cit.*, p. 17.

⁷ *Ibid.*, p. 118.

drosses, old solder, bronze, sweepings, etc. From these materials the recovery of tin is commonplace and expected, except from used tin cans; in them the loss of tin is enormous, and in the recovery of tin from them must be the future growth in the comparative percentage of waste material treated.

At present the Vulcan Detinning Company is recovering tin from a considerable quantity of used tin cans. In a small way cans are treated by others for recovery of their solder. A common method of recovery is to throw the cans into a small sheet-iron vertical cylinder in which is a wood fire; such solder as runs down into the ashes is collected and remelted into more salable form.

The tin recovered during the year as tin amounted to 2,423 short tons; in the form of alloys, such as solder, babbitt metal, bronze, etc., 3,092 short tons were recovered, a total of 5,515 tons, equal to more than one-ninth of the tin imported into this country and worth at the average price for the year (about 29.75 cents per pound) \$3,281,425. Besides the money value involved, the world's tin resources were increased by so much—a very real conservation.

In Europe there was also a large saving of tin from various wastes, but the quantity is unknown.

ANTIMONY IN 1909.

No production of antimony ore in the United States during 1909 has been reported to the United States Geological Survey. There was, however, a considerable quantity of antimonial lead produced as a by-product in the smelting of other metals and in the refining of pig lead by the electrolytic process. As most of the antimony used goes into lead alloys, antimonial lead is a convenient form in which to handle antimony and there is no necessity for separating it from the lead. Besides the production of antimonial lead, a large quantity of antimony was recovered from various wastes, such as drosses, residues, old type, babbitt metal, journal bearings, etc.¹ Of this quantity, about 27 tons was recovered as antimony and 1,529 tons was recovered as a component of various alloys, a total of 1,556 tons of recovered antimony. Reports were received from 23 companies.

The production of antimony in the United States since 1903 has been as follows:

Imports of antimony and antimony compounds entered for consumption during 1909 were large. The imports of antimony metals and regulus, 9,557,956 pounds, were larger than in 1908 and practically equal to the imports for 1907; but the value, \$620,117, was less than that of the smaller quantity imported in 1908 (8,089,915 pounds, valued at \$771,206), and not half of the value of the nearly equal quantity imported in 1907, when imports of 9,600,901 pounds were valued at \$1,407,861.

¹ Figures collected by John P. Dunlop, of the United States Geological Survey.

² Estimated from the average content of the ore.

³ Estimated from the prices current for the year.

⁴ Figured as 60 per cent. of domestic ores only; direct figures from the smelters could not be obtained.

⁵ Estimated, using 16.3 cents as the average price per pound.

⁶ Estimated, using 8 cents as the average price per pound.

⁷ None produced from domestic ore. Figures not collected for foreign ores.

⁸ Estimated, using 7.8 cents as the average price per pound.

In the following table the imports of antimony and antimony ore for consumption are given since 1899 in order to show the great variation in both quantity and value of the imports from year to year. Importations of salts of antimony are given only since 1903, the earliest year for which the Survey has obtained statistics:

ANTIMONY, ANTIMONY ORE, AND SALTS OF ANTIMONY IMPORTED AND ENTERED FOR CONSUMPTION IN THE UNITED STATES 1899-1909 IN POUNDS

Years.	Metal and regulus.		Crude antimony and ore.		Oxide and salts of antimony.		Total value.
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.	
1899.....	2,990,915	\$241,685	3,968,654	\$47,427	\$289,112
1900.....	3,654,822	287,937	6,089,134	75,866	363,803
1901.....	3,640,505	254,529	1,682,301	22,720	278,066
1902.....	5,388,739	333,601	3,129,069	62,968	396,569
1903.....	4,694,309	260,144	2,714,617	54,316	916,468	\$66,469	380,929
1904.....	4,268,045	248,726	2,488,518	50,414	981,026	70,668	369,808
1905.....	4,941,247	431,228	1,970,788	53,026	1,010,228	80,130	564,384
1906.....	10,305,734	1,391,289	1,972,658	125,841	764,070	99,251	1,616,279
1907.....	9,600,901	1,407,861	2,771,387	180,903	682,192	98,038	1,686,802
1908.....	8,089,915	771,206	3,287,218	106,930	623,125	65,898	744,034
1909.....	9,557,956	620,117	3,453,542	94,249	955,360	60,353	774,719

The apparent consumption for the year is the sum of the antimony imported, smelted from imported crude antimony and ore, produced in antimonial lead of both foreign and domestic origin, and recovered from secondary sources, such as old alloys, scrap, etc. If the recovery from imported crude antimony and ore is taken as about 50 per cent. of the gross weight, the sum of the items named is 9,558 tons. This is exclusive of the antimony contained in oxide and salts, which would probably add 200 or 300 tons more.

The real consumption would have to take into account the stocks of antimony held at the beginning and the end of the year, and the imports and exports of type metal and of other antimonial alloys.

The price of antimony was fairly steady during 1909. According to the annual statistics issued by "The American Metal Market," of New York, the year opened with an average price for Cookson's of 8.11 cents during January. The price dropped until it averaged 7.95 cents during March. There was then a gradual rise, and during August the average price was 8.55 cents. Prices then gradually dwindled until November, during which month and December the average price per pound was 8.375 cents. The average price of Cookson's for the year was 8.27 cents per pound. Other brands were one-eighth to one-half cent less per pound.

ARSENIC IN 1909.

In 1909, as in 1908, the only arsenic produced in the United States was the recovered in the form of white arsenic (As_2O_3) as a by-product in smelting. During 1909 white arsenic was saved at three smelters. Besides the arsenic-saving plant of the American Smelters Securities Company, at Everett, Wash., and that of the Anaconda Copper Mining Company, at Anaconda, Mont., a new plant was put up by the United States Smelting Company, at Midvale, Utah. The last company, which began producing during the year, smelts large quantities of Utah lead ores, which are highly arsenical, and from the flue dusts made in smelting these ores the arsenic is saved.

The arsenic mines at Brinton, Floyd County, Va., and at Mineral, Wash., did not operate, owing to the low price of white arsenic.

The total quantity of arsenic saved by the three smelters during 1909 amounted to 2,428,313 pounds or 1,214 short tons, valued at \$52,946. The average prices received by the companies ranged from 2.05 to 2.4 cents per pound. The price in New York ranged around 3 cents per pound. The highest average monthly price was 3.25 cents per pound in January; the

lowest, 2.725 cents per pound in October. The average price for the year was 2.97 cents per pound.¹

The United States imported much more arsenic than it saved during the year, but most of the imported arsenic was in the form of sulphide.

The production and importation of arsenic, white arsenic,

and arsenic sulphides and of Paris green and London purple since 1901 are given in the following table:

PRODUCTION AND IMPORTS OF ARSENIC, 1901-1909.

Years.	Production of white arsenic.		Imports.			
			White arsenic, metallic arsenic, and arsenic sulphides.		Paris green and London purple.	
	Quantity (short tons).	Value.	Quantity (short tons).	Value.	Quantity (pounds).	Value.
1901.....	300	\$18,000	3,495	\$316,625
1902.....	1,353	81,180	4,055	280,055
1903.....	611	36,691	4,179	294,602
1904.....	36	2,185	3,400	243,380	28,498	\$985
1905.....	754	35,210	3,838	256,540	44,931	1,118
1906.....	737	63,460	3,987	350,045	311,293	21,347
1907.....	1,751	163,000	5,164	574,998	133,422	21,919
1908.....	(?)	...	4,964	430,400	195,000	30,764
1909.....	1,214	52,946	4,036	303,728	183,765	20,370

The imports came from Canada, Europe and Mexico.

A large part of the white arsenic produced and imported is made into Paris green for use as an insecticide. The prices for Paris green have been held at high figures by the few manufacturers. Prices are said to be fixed in advance of the season. During 1909, prices from January to the middle of July, as quoted by the *Oil, Paint, and Drug Reporter*, of New York, were as follows:

PRICES OF PARIS GREEN DURING 1909, NEW YORK, CENTS PER POUND 1909.

	Before July 15.	July 15 to Dec. 31.
In bulk.....	21 ½	17
100-pound to 175-pound packages.....	22	17 ½
14, 28 and 56-pound packages.....	23	18 ½
2- and 5-pound packages.....	23 ½	19
1-pound packages.....	24 ½	20
½-pound packages.....	25 ½	21
¼-pound packages.....	26 ½	22

The cause of the fall in prices is not altogether clear, but the formation of a company to establish an independent factory at Norfolk, Va., which was to make Paris green from white arsenic made at the Brinton (Va.) arsenic mine, was nearly coincident with the decline.

Paris green is protected by a duty of 15 per cent. *ad valorem*.

BISMUTH IN 1909.

Production.—The only production of bismuth in the United States during 1909 reported to the United States Geological Survey was made by the United States Metals Refining Com-

¹ *Eng. and Min. Jour.*, 89, 137 (1910).

² There were only two producers of arsenic in the United States in 1908, so that the figures of production may not be given.

pany as a by-product at its electrolytic lead refinery (Betts process) at Grasselli, Ind. The bismuth is obtained from the anode muds of lead bullion. The bullion comes largely from the Utah lead ores smelted at the company's plant at Bingham Junction, Utah. Most of the lead ores carrying bismuth come from the Tintic district, but the company buys bismuth-bearing lead, gold and silver ores from other districts and States. More was recovered in 1909 than in previous years. As the output is that of a single firm, the figures may not be disclosed.

The Monsanto Chemical Company's electrolytic lead plant at St. Louis was idle during 1909. It was built to operate on bismuth-bearing bullion from Mexico, but the bullion produced at the mine on which it expected to draw was sent to England for refining.

Many tungsten ores carry bismuth, and one company is known to save it as a by-product when reducing the tungsten. Some bismuth is recoverable in the electrolytic copper refineries and experiments have been carried out toward this end, but no saving has yet been reported to the United States Geological Survey. It seems entirely possible that the United States may, in time, put its markets beyond foreign domination by saving the bismuth which at present goes to waste in various smelting industries.

Bolivia is the principal bismuth-producing country, and from it, during 1909, bismuth ore amounting to 481,215 pounds, valued at \$188,574, were exported.¹ Smaller quantities were produced in Queensland, New South Wales, and Tasmania.

Other countries that are either actual or possible producers of bismuth are Bohemia, Mexico, Norway, Peru, Portugal, Saxony, and Spain.

Imports.—The imports of metallic bismuth for consumption during the last six years have been as follows:

IMPORTS FOR CONSUMPTION OF METALLIC BISMUTH INTO THE UNITED STATES, 1904-1909, INCLUSIVE, IN POUNDS.

Years.	Quantity.	Value.
1904.....	185,905	\$339,058
1905.....	148,589	318,007
1906.....	254,733	318,452
1907.....	259,881	325,015
1908.....	164,793	257,397
1909.....	183,413	286,516

Prices.—The price of bismuth and its compounds is closely governed by foreign firms. During 1909 the price of bismuth through the whole year was quoted at from \$1.70 to \$1.80 per pound. If the price of bismuth were materially reduced, the use would undoubtedly largely increase. Throughout the year 1909² bismuth compounds sold as follows, per pound: the citrate, \$1.85 to \$1.90; the salicylate, \$1.25 to \$1.30; the subcarbonate, \$1.65 to \$1.70; the subgallate, \$1.35 to \$1.40; and the subnitrate, \$1.40 to \$1.45.

SELENIUM IN 1909.

Selenium is known to have been made during 1909 at only one place in the United States, where a comparatively small quantity was saved. It was sold at an average price of \$3.43 per pound. The uses are at present very limited, and should they so increase as to create a demand for large quantities of the element, it could be profitably sold at a much lower price. As the output is that of a single company, the figures of production may not be given.

MERCK & CO'S NEW QUARTERS.

Merck & Co. have moved into new quarters at 45 and 47 Park Place, Manhattan, after fourteen years spent in the Merck Building at University Place and Eighth Street. This move into the wholesale business center of New York, near the Hudson

¹ Figures furnished by the Bureau of American Republics, Washington, D. C.

² *Paint, Oil and Drug Reporter*, weekly prices.

Terminal buildings, has been in contemplation ever since the Merck works were established in Rahway, N. J. The new location is within three minutes' walk of the Jersey ferries, so that office and factory are brought into close connection. The firm's auto truck service several times daily between New York and Rahway effects a considerable saving in time by reason of the change.

Besides being in close proximity to the McAdoo tunnels and the west-side ferries the new Merck headquarters are only a half block from the Sixth Ave. L, and are within a few minutes walk of the subways, the Brooklyn Bridge, the General Post Office, and are hardly more than a block from Broadway.

Merck & Co. have a tract of 120 acres at Rahway, a considerable portion of which is already taken up by their extensive works, warehouses, and the cottages of superintendent and chemists. Here the shipping facilities are of the best, with a half-mile of railroad sidings alongside the main tracks of the Pennsylvania Railroad.

The western branch office of Merck & Co. remains at St. Louis, Mo.

PHOSPHORUS SUBSTITUTE PATENTS.

It is stated that the American Association for Labor Legislation has induced the Diamond Match Co. to assign its patent for the most available substitute for poisonous phosphorus in the manufacture of matches to three trustees: Prof. Seligman of Columbia University, and Commissioner Neil and Attorney Ralston of Washington. The trustees are empowered to deal with all future applicants who may wish to use the substitute in such manner as they may think just. The Esch phosphorus bill, which was prepared by the American Association for Labor Legislation and later endorsed as to method by President Taft in his recent message, at this writing is not reported out of the Ways and Means Committee.

TURPENTINE AND TURPENTINE SUBSTITUTES.

ENGLAND.

(From Consul-General John L. Griffiths, London.)

There are a number of substitutes for turpentine upon the English market, the price ranging, according to a local dealer, from 24 cents to within a few cents of the price of pure spirits of turpentine. The bulk of these substitutes is sold direct to the painters and paint manufacturers, who do not guarantee their paints as mixed with pure spirits of turpentine. The manufacture of these substitutes has been in progress for a long time, and is particularly active when the price of turpentine goes above 50 cents per gallon in the United States.

The imports of turpentine into the United Kingdom during 1909 amounted to 589,880 hundredweights of 112 pounds, valued at \$3,405,610. Of this amount the United States furnished 476,484 hundredweights, valued at \$2,979,875; Russia, 77,382 hundredweights, valued at \$242,585; France, 31,084 hundredweights, valued at \$150,117; Germany, 2,290 hundredweights, valued at \$6,399; and other countries, 2,640 hundredweights, valued at \$26,634. (A list of importers and dealers in turpentine is filed for reference in the Bureau of Manufactures.)

(From Consul Horace Lee Washington, Liverpool.)

Regarding the prospects of introducing a turpentine substitute into this market, it appears from inquiry made of several firms, who handle the larger part of the imports of paint, turpentine, etc., in Liverpool, that substitutes for turpentine are manufactured by many of the distillers in this locality. A substitute which is well thought of by the trade, and which is manufactured in this country, commands a good sale at the price of \$136.26 per ton, f. o. b. Liverpool. The imports of turpentine into Liverpool from the United States in 1909 amounted to 48,422 hundredweights, valued at \$390,823.

(The names and addresses of the firms who do a large business in turpentine are listed for reference in the Bureau of Manufactures.)

SOUTH AFRICA.

(From Consul Edwin N. Gunsaulus, Johannesburg.)

There is considerable sale for turpentine substitutes in this market owing to the prevailing high price of turpentine. With good local agencies it would appear that a satisfactory trade might be established by those not selling such products in this territory, while those already in the market should be able to increase their sales.

It should be borne in mind that shipment of goods of this description must be in tins, known as "American packing," and not in barrels. The packing is usually in tins of 5 gallons each and smaller, as required. (A list of some of the leading importers and dealers in turpentine and similar products in this district is on file in the Bureau of Manufactures.)

SWITZERLAND.

(From Consul George Heimrod, Berne.)

The imports of turpentine oil into Switzerland in 1909 amounted to 3,044,260 pounds, distributed among the following countries: United States, 13,660; Belgium, 8,150; France, 1,518,000; Spain, 1,515,000; Austria-Hungary, 440; England, 660; Germany, 5,950; and Italy, 2,400. The average price delivered at the Swiss boundary was \$15.63 per 220.46 pounds. There is no customs duty. The oil is usually shipped in metal receptacles containing 352.7 pounds and its specific gravity is 900. (Names of dealers at Berne may be obtained at the Bureau of Manufactures.)

JAPAN.

With reference to the experiments in turpentine extraction in Karafut (Japanese Sakhalin) the British consul at Hokodate reports that, preliminary experiments having proved very successful, the manufacture of turpentine by the Government is shortly to be begun. Machinery for the purpose to the value of about \$75,000 has been ordered. It is hoped eventually to produce a very large amount of turpentine, as the sources of supply are almost inexhaustible, and consequently more machinery will doubtless be required later. In connection with the manufacture of turpentine at the government laboratory, experiments are to be made in the manufacture of gun-cotton. The consul has forwarded to the British Board of Trade at London samples of raw turpentine, extracted from the tree "*Larix dahurica* Turcz.," known in Karafuto as the "Rakuyosho," of refined turpentine oil produced at the government experimental laboratory and of the rosin left after the extraction of the oil.

ALCOHOL FROM THE CAROB BEAN.

(From Consul General Henry H. Morgan, Barcelona, Spain.)

The discovery that alcohol can be extracted from the fruit of the carob tree has caused this article to be looked upon as much more valuable than formerly. This tree is a leguminous evergreen found in Spain, Italy and the Levant, and its fruit, commonly called the "carob bean," is about 1 inch wide and from 6 to 8 inches long, and when dried has hitherto been used as food for animals.

Experiments have lately been made in Spain to obtain alcohol from this bean. After triturating the fruit it was immediately placed in hot water to steep and the sugar or glucose extracted by means of a current of water. The liquid resulting from the process was then allowed to ferment, the glucose thus being transformed to alcohol, which was later distilled. It was found that 2.3 quarts of pure alcohol could be obtained from 22 pounds of the beans.

A factory has been established at Faro, in Portugal, furnished with a triturator of 4,408 pounds capacity per hour. Here the practice is to steep the beans in four or five times their weight of water at 70° C. for one hour. The quantity of water depends upon the amount of glucose contained in the beans, which must be determined chemically. In the Faro factory 3 to 5 per cent. of sulphuric acid are added to the water. The sugared liquid is fermented by adding the leaven of figs or beer, usually the latter. The fermentation, which takes three days, is made in wooden casks at 25° C., and is very tumultuous. The distilling is with the most modern apparatus, because the alcohol from the carob bean, unless very pure, emits a peculiar odor and has a disagreeable taste.

Owing to the great quantity of carob trees (*algarrobos*) in Spain, this discovery will likely establish another important industry in this peninsula, as well as in other Mediterranean countries. Large quantities of the bean are grown in this district and in the Provinces of Valencia and Castellon, and in the south the production is even greater. It is used chiefly as food for horses, sheep, and goats, and the current price is 90 cents per hundredweight.

MANUFACTURE OF CELLULOID IN JAPAN.

(From Consul George N. West, Kobe.)

There are two plants in course of erection in Japan for the manufacture of celluloid, one of which, located a few miles from Osaka, is expected to begin operations during the present month (November), and the other, located at Aboshi, which is now installing its machinery, is expected to be completed by the end of December.

According to the *Japan Chronicle*, the two companies show a wide divergence of opinions as to the success of this new undertaking. The Aboshi company's opinions as expressed in the *Chronicle*, are as follows:

One of the principal materials used in the manufacture of celluloid can not be obtained in Japan and has to be imported entirely from Germany. Neither can the nitric acid or strong alcohol required be produced in Japan. When celluloid made in Japan from material imported from Germany is exported to China, India, and other countries, the freight and customs duty on the product amounts to 12 sen (6 cents) per pound. Under these circumstances it will cost more to produce celluloid in Japan than in Germany.

The Osaka Company holds that—

The principal materials required for celluloid can be procured in Japan cheaper than in Germany. Alcohol strong enough to meet the requirements for the industry can be produced in Tokyo. Of the materials necessary for the production of celluloid, it is contended that nitric acid is the only one that must be imported from abroad. In these circumstances the cost of raw materials will be smaller in Japan than in Europe. This advantage, combined with the lower price of labor in Japan, will, it is thought, place the Japanese product in a position to successfully compete with the foreign product in the oriental market.

POSSIBLE EFFECT ON THE AMERICAN INDUSTRY.

The first company holds that the cheaper labor in Japan can not compensate for the higher price of materials which must be imported, and that state aid, in some form, will be necessary for the success of the new enterprise.

It is apparent that if the manufacturers here are successful, and that celluloid can be produced in Japan at less cost than in the United States, either through state assistance or through the Japanese being able to secure camphor, which so largely

enters into the manufacture, at a less price than is paid by the American manufacturers, the industry of the latter will be seriously affected.

NITRATE INDUSTRY OF CHILE.

According to the report it is estimated that the nitrate fields of Chile contain 242,150,000 tons of 2,000 pounds, and that, with an annual exportation of 2,000,000 tons, they can supply the world's consumption for 120 years.

The annual exportation of nitrate from Chile has been, in tons of 2,000 pounds: 1,814,585 tons in 1907, 2,236,973 tons in 1908, and 2,319,571 tons in 1909, of which the United States took 132,570 tons in 1907, 369,294 tons in 1908, and 503,889 tons in 1909. Unofficial figures for 1909 and 1910 show a consumption by the United States of 639,949 tons, which represents an enormous increase.

NITRATE PRODUCTION ORGANIZED.

(From Consul Alfred A. Winslow, Valparaiso, Chile.)

The nitrate of soda producers of Chile have an organized Nitrate Propaganda working to increase the consumption of nitrate of soda throughout the world. During the nitrate year ended June 30, 1910, the propaganda expended \$438,000 (United States gold) in this work, the Government of Chile contributing \$195,000.

From the following table it will be seen that the propaganda succeeded in increasing the exports for 1909-10 about 25 per cent. over those for 1908-9, and from reports since July, 1910, it would seem that the association's work continues effective. The following export figures represent Spanish quintals of 101.6 pounds each:

Country.	1908-9.	1909-10.
Argentina.....	21,978	21,875
Australia.....	15,400	75,600
Austria-Hungary.....	136,525	72,825

Country.	1908-9.	1909-10
Ecuador.....	163	448
Belgium.....	1,177,885	2,295,046
Bolivia.....		32
Brazil.....	3,269	4,183
British Columbia.....	189,728	215,194
Chile.....	26,708	23,316
China.....		14,190
France.....	2,244,120	1,477,476
Falkland Islands.....		22
Egypt.....		235,755
Germany.....	9,661,896	13,801,523
Great Britain.....	15,276,071	16,670,308
Holland.....	1,589,336	1,759,061
India.....		11,000
Italy.....	339,369	496,931
Japan.....	56,100	259,050
Mediterranean countries n. e. s....	391,562	611,272
Mexico.....	11,000	76,960
Panama.....	66	6
Peru.....	10,427	5,709
Sandwich Islands.....	190,582	443,139
Spain.....	330,580	193,982
Sweden.....	55,000	53,800
South Africa.....	537,396	490,596
United States.....	7,988,121	12,672,262
Total.....	40,263,282	51,981,561

The nitrate interests do not seem to be quite satisfied with the result and propose to expend \$500,000 next year to further extend the business. (A list of the permanent nitrate committee is filed for reference at the Bureau of Manufactures.)

CORRECTION.

In my note on "Dissolving Silicon Alloys" in the January, 1911, issue for "(21 per cent. Si; 39 per cent. Mn; 42 per cent. Cr)" read "(21 per cent. Si; 39 per cent. Mn; 0.42 per cent. Cr)."



CHARLES MARTIN HALL,
RECIPIENT OF PERKIN MEDAL



PERKIN MEDAL 1911

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EDITORIALS.

JOURNAL.

The editorial work of the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY is a great responsibility, and one not undertaken without serious misgivings. While technically, the burden of this responsibility is placed upon the Editorial Board, it must be perfectly obvious that in a journal which is the official publication of a large organization of professional men, from which the members of the editorial board are chosen, and for which they serve without compensation, a great share of this responsibility attaches to every member of the Society.

The committee appointed by the President of the Society, to consider and report upon the policy of the INDUSTRIAL JOURNAL, strongly recommended a broadening of the field of its operations, and urged that it build up a world-wide staff of correspondents to report upon industrial achievements, processes, and general scientific matters. They also advised that the policy of the JOURNAL be broadened to afford a medium for the discussion of topics of chemical and engineering interest, as well as for the publication of original contributions, thereby enhancing the value of the JOURNAL to the members of our profession whose time and facilities do not permit of a general review of the industrial press.

We believe that the report of the committee outlines a policy, which is not only feasible, but highly de-

sirable, and that the conduct of the JOURNAL along the lines suggested will give the best value to those engaged in, and interested in, the applications of chemistry.

An individual editor, or a board of editors, could not hope to initiate and execute the committee's policy without the coöperation of the individual members of the Society. Even if such a plan were feasible, the difficulty of having one, or a few men direct the policy of such a journal and control its infinite variety of interests is manifestly great. This is especially true when we consider that the readers are not the usual gullible public digesters of popular science magazines, but are experts in the lines of endeavor properly undertaken by the JOURNAL, and are trained to analyze and examine to the greatest degree of exactness.

The editors believe that the standard of the JOURNAL in every respect—original contributions, notes, news, correspondence, and advertising—must be of the highest order, and their efforts will be directed to that end.

The existence of an organ of applied chemistry is assured as long as it is promoted by the American Chemical Society; but THIS JOURNAL should have more than an existence. Owned and operated by its readers, it must commend itself to the support of its readers, and thereby pass from a mere existence to a position eminently representative of the organization.

Practically every member of the Society is engaged in, or interested in, the application of chemistry to great industrial problems, and it is only through the constructive suggestions, the contributions, the support, and the coöperation of every chemist of the organization, that the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY will be able to keep pace with the rapid industrial development of the country and the profession.

FACTORY EFFICIENCY.

The statements of Mr. Brandies before the Interstate Commerce Commission a few days ago, that the railroads of the United States could save at least \$1,000,000 dollars a day by applying the well-known principles of scientific management, has been given wide publicity and has caused much discussion.

Entirely apart from the question of the correctness of this sensational statement, it has another element of value if it will bring home to men in positions of responsible management the thought that perhaps wonderful results might be attained in the industries they direct, if they should study and develop the principles involved in the so-called "Scientific Management."

In a line of manufactures where the labor is less than 20 per cent. of the cost of production, for example, rubber goods, brass, etc., a scientific study and a systematic correction of the unnecessary and useless movements of each machine operator and each employee naturally would not produce very striking results. The scientific methods should be first directed at the material wastes and losses and the operating and expense items, or to that portion of the factory which contributes the largest proportion to the cost of production. Obviously, if large results are to be obtained, such methods might be applied to the best managed factories in the country with profit, while in many of our plants the applications of the scientific studies which lead to the highest efficiency have not been undertaken at all.

The term "Scientific methods" sounds more formidable than it really is. To be sure, in a great many cases in factory management, improved efficiency is based on the application of sound—though not always profound—chemistry, physics, mechanics, thermodynamics, psychology, etc. In a great number of other cases it is based upon the consistent application of that extra college attainment—"horse sense." An example of the latter may be cited in which a manager noticed that all orders on works stores for expense supplies, such as soap, oil, waste, repairs, renewals, etc., were signed by the office boy, using the superintendent's autograph rubber stamp. Presumably, the various departments were not using any more of these supplies than they needed; nevertheless, the impersonal way in which the orders were put through, made direct responsibility easy to evade. The manager decided to apply the "horse sense" phase of "Scientific management." All rubber stamps about the works were collected and sent to the boiler room, with instructions to the firemen to realize on their heat value. Each department foreman was advised to sign his own orders for anything he wanted—and only his own. Individual ledger accounts were then opened in the office for each foreman, his department being charged at the purchase price with every order he signed. Transcripts of these accounts were given to each foreman monthly. As soon as it became apparent to the foreman that he had a personal responsibility, there was not only a marked falling off in the amount of material ordered, but the purchase price was noted, and the purchasing office given the benefit of many suggestions which resulted in more careful buying. The net result of this transfer of responsibility from the impersonal rubber stamp in the hands of the office boy to the foreman personally was the addition of \$35,000 dollars per year to the profits of the works.

No manager would be quick to admit to the public, or to the lay stockholders, that great changes and improvements could be made in the efficiency of his plant operation; but every manager admits to himself, when confronted with impending tariff changes, or growing foreign and domestic competition, that he must look for means to reduce the cost of production. The cost of selling increases with the severity of com-

petition, and this adds an additional burden, which must be shouldered by the factory if profits are to be maintained.

The application of the "Scientific method," as interpreted in connection with improved factory efficiency, does not involve a profound scientific research, but invokes the use of the "eagle eye" of a sensible man to every nook, corner, operation, and product of the plant, with special attention to the coal pile, the drainage sewers, and the factory gates—the three great escape valves for chemical factory profits.

Such a study, and the application of remedies based upon sound scientific principles, will give profitable results of a surprising magnitude in many, if not all factories, and will suggest the solution for great problems of factory development in the face of falling prices and increasing competition.

DR. RICHARDSON.

It is a matter of regret that Dr. W. D. Richardson, who has been head of the editorial staff of the JOURNAL since its organization, could not be induced to continue the responsibilities of that position. His withdrawal from the chief editorship will not entirely deprive us of his services and advice, as he has consented to devote a portion of his time and interest to the JOURNAL in the capacity of an associate editor.

The Society owes a debt of gratitude to Dr. Richardson for his services in organizing the JOURNAL, and administering its affairs during its infancy.

LEONARD PARKER KINNICUTT.

Dr. Leonard P. Kinnicutt, an associate editor of THIS JOURNAL since its beginning, a leading authority in sanitary chemistry, especially sewage disposal and water supply, and director of the department of chemistry of the Worcester Polytechnic Institute, died at his home in Worcester on February 6th in his fifty-seventh year, after an illness of several months.

A graduate of the Massachusetts Institute of Technology in 1875 he then studied in Germany until 1879, at first with Bunsen at Heidelberg, where he was a fellow student of Treadwell, now of Zurich, and Bedson, of Newcastle on Tyne, then at Bonn with Kekulé and Anschütz, with Japp and Richardson as fellow students. He returned to this country in 1879 and spent a year at Johns Hopkins, going from there to Harvard where he remained for three years, taking the degree of Sc.D. and serving as instructor in quantitative analysis. In 1883 he was appointed assistant professor at Worcester, and became a full professor in 1886 and director of the chemical department in 1892, the position he filled at the time of his death.

With the establishment of sewage disposal works in Worcester his attention was drawn to sanitary problems and he devoted the remainder of his life to them. He was recognized, both at home and abroad, as a leading authority on such subjects, as is shown by the fact that he had been chosen as vice-president of the

section of hygiene of the coming International Congress of Applied Chemistry.

Much of his time after 1885 was devoted to the study of the contamination of rivers and ponds by trade waste and sewage, with special attention to their pollution by wool washings, in connection with the Blackstone River at Providence, R. I., by the waste of the Wamsutta Mills, the Ware River in Massachusetts by that of the Barre Wool Combing Co., and pollution of the same character at Bradford, England, where a greater amount of wool is washed annually than in any other city in England or America. He was employed as an expert in numerous cases where the pollution of streams and ponds was under consideration, such as Saratoga Lake, the Nashua River at Clinton and at Fitchburg, the Assabet River at Westboro, and the water supplies of Webster, Quincy, Millbury, Worcester, Warren, Bristol, Gardner, Athol and Jersey City. He was one of the principal experts for the city of Chicago in the case of "The State of Missouri *vs.* the State of Illinois and the Sanitary District of Chicago," which he successfully defended, and in the well-known Passaic Valley case, "Jersey City *vs.* Jersey City Water Supply Co.," where he was the expert for the Water Company.

Because of the fact that his personal engagements took him over such a wide field, and because it was his habit to spend his vacations every other year in England and on the Continent familiarizing himself with the work that was done abroad, and with the leading experts there, Dr. Kinnicutt was a man of very broad horizon. He was more generally known on the other side of the ocean as a sanitary chemist than any of our experts.

As a teacher Dr. Kinnicutt met with the same success as in other walks of life. As a member of the institute faculty he was most popular with his students. A touching tribute to him appears in the editorial column of the *Tech News*. It says, in part:

"He was a friend of the students but particularly of the struggling student. His words of advice and his help financially (though generally not publicly known) have strengthened the heart of many a struggling student and has been the means of enabling students to obtain an education. We miss him; we miss his personality; we miss the man of great heart, of wonderful industry, of untiring devotion."

Dr. Kinnicutt's attractive personality appealed as strongly to his professional associates as to his students, and his presence was always welcome at all the scientific meetings which he attended. He was at once the heart and soul of good fellowship. No loss in the ranks of chemists will be more felt than that occasioned by Dr. Kinnicutt's death.

CLIFFORD RICHARDSON.

THE PERKIN MEDAL AWARD.

The Perkin Medal was conferred upon Charles Martin Hall for his inventions and discoveries in connection with the manufacture of aluminum, by the New York

Section of the Society of Chemical Industry at its regular meeting, January 20, 1911.

The Perkin Medal Award is determined by the committee representing the Society of Chemical Industry, The American Chemical Society, and the American Electrochemical Society. This medal, founded in commemoration of the fiftieth anniversary of the coal tar industry, is awarded to a chemist residing in the United States, for valuable work in applied chemistry, and especially work which has become valuable in the future development of a great industry.

Mr. Hall's discoveries and inventions were regarded by the committee as of a distinctly high order, and the award was recommended by a unanimous vote. His discovery that aluminum oxide dissolved in fused cryolite, producing a solution of low electrical conductivity, from which he could deposit the aluminum in the metallic state, is the basis of the aluminum industry.

Mr. Hall has also made many other valuable inventions, both in the field of chemistry and its engineering applications, which have an important bearing on the metallurgy of aluminum.

The wisdom of the committee in awarding the medal to Mr. Hall was substantially endorsed by the large attendance at the exercises and the enthusiasm shown by the audience. Interest was enhanced by the presence and participation in the exercises, of Paul L. V. Héroult, who simultaneously made the same discoveries in Europe as those made by Mr. Hall in America.

As a result of the independent discoveries of Hall and Héroult, the European rights in the aluminum industry have been enjoyed by Mr. Héroult and the American rights by Mr. Hall.

An abstract of the official report of the proceedings is an interesting contribution to the literature of the aluminum industry, and shows the cordial professional endorsement given to the meritorious inventions made by Mr. Hall.

OPENING ADDRESS OF DR. CHARLES F. MCKENNA, *Chairman*: The foundation of the Perkin Medal was a happy act of scientific benevolence. Perkin's contemporaries in America, wishing to do something which would honor him in life and continue to keep his memory illustrious in science, even after he should have passed away, chose to establish this medal and to see to it that in recurring years it should go as a reward to the men who had struggled, striven and fought and forced nature to yield further favors to men.

Sir William Perkin has passed away and yet each year his achievement stands out bolder on the pages of chemical history; each year the new award of this medal adds a link to the chain connecting the great work of industrial chemical advancement in America with the earliest and most pronounced advance made in England when aniline yielded up mauve. Each year the appreciation of this honor grows, and the annual award of the Perkin medal is coming to be looked upon as the *concours* of chemical industry.

The thoughtful men who, in founding this benev-

olence drew up its guarantees and conditions, builded carefully, and perhaps better than they knew. Besides leaving the selection of the recipient open to nomination by a large group of American societies interested in chemistry, they placed no restriction as to the period in which the discovery may have been made. This leads to careful judgment and brings forward for the palm many a struggling chemist who, in years past, had known the disadvantages of inconspicuousness, and the hardships of passing along the dusty road of conflicting interests.

It happened that the importance of Sir William's discovery was immediately grasped and that it spread quickly throughout the world. But this is not always the case in our chemical discoveries, and I think it can be said that the full appreciation of the significance of an American college student's experiments in electrolyzing a solution of alumina in fused cryolite was long in dawning.

Therefore we must rejoice that the Perkin Medal gives the chemical fraternity the opportunity to honor one of our confreres whose modesty has been as singular as his patience has been marked.

I must call attention to a most happy coincidence occurring here to-night. We all know that we have come here to give the palm to one who labored in the metallurgical winning of aluminum. What is more appropriate than that the one who extends it to him should be the dean of our profession and next to the oldest living pupil of Wöhler who first isolated aluminum, our foremost American teacher—an enthusiast himself over aluminum, the preceptor who inspired Castner to toil over the smelting of sodium that the smelting of aluminum might follow, the friend of the struggling inventor and the guardian of his rights? It is in the rules prescribed that the presenting officer shall be the senior Past-President of our society resident in the United States, and, as I have just stated, how happy we are to be able to introduce to you in the person of that officer, Dr. Charles F. Chandler.

DR. CHARLES F. CHANDLER: *Mr. Chairman and Brother Chemists:* It is my privilege and very pleasant duty, as the senior Past-President of the Society of Chemical Industry residing in this country, to present to Charles Martin Hall, LL.D., the fifth impression of the Perkin Medal in recognition of his most valuable work in applied chemistry.

This work relates particularly to his discoveries and inventions in connection with aluminum. This is a subject which has interested me deeply from my student days. In 1854 I listened to Wöhler's account of his discovery of aluminum in 1827, and the following year (1855) I was shown by Rose aluminum which he extracted from cryolite by the action of sodium—and that was the first time cryolite had appeared out of Greenland in any form, except as a rare specimen—in the spring of that year. In 1869 I had the pleasure of making the acquaintance of Henri St. Claire Deville, in Paris, who in 1854 and the following years prepared aluminum on a manufacturing scale. Later, I had among my pupils in the School of Mines my warm friend Hamilton Y. Castner, who for two years mon-

opolized the manufacture of aluminum by means of his cheap sodium; and, finally, for the past twenty years, I have been very intimate with Dr. Hall, whose electrolytic process at Niagara Falls has produced the metal in such enormous quantities and at such a low price that it has monopolized our market, and taken the place, for innumerable purposes, of other metals formerly employed.

The name "aluminum" is derived from alumen, which included alum, in which Margraf, in 1754, recognized a peculiar earth, which we call alumina, and which was supposed, a century ago, to contain a metal. Sir Humphry Davy, who in 1807 succeeded in extracting sodium from soda and potassium from potash, and a little later the metals of lime, magnesia, glucina and strontia, endeavored to reduce alumina, by heating, with the aid of 1000 galvanic couples, an iron wire in contact with alumina in an atmosphere of hydrogen. The iron fused became whiter and on solution in acid yielded alumina. He evidently produced an alloy of iron and aluminum. Nothing further was done till 1827, when Wöhler reduced aluminum chloride with potassium, and obtained aluminum as a gray, metallic powder, and later, in 1845, by acting on aluminum chlorides with potassium vapor, obtained the metal in tin-white globules.

In 1854 Henri St. Claire Deville became imbued with the idea of making aluminum a useful metal. He secured the interest of the Emperor Louis Napoleon, and with liberal grants of money was able to work on a factory scale. He employed aluminum chloride and sodium, thus modifying the process of Wöhler by substituting sodium for potassium, and he introduced many improvements in the processes for their preparation and application, and manufactured the metal in what, for those days, seemed very large quantities.

I emphasize "cryolite" because it was to cryolite that the guest of the evening owed his discovery. St. Claire Deville used cryolite as a flux. This mineral from Greenland was used experimentally to produce aluminum by the action of sodium in 1855 by both Rose and Percy. Deville's factories continued to produce aluminum on a moderate scale till about 1888, reaching a maximum output of over 5,000 pounds per annum. That represents the maximum production of aluminum in Deville's days. A few other manufacturers established works. The process of manufacture was, however, so expensive that aluminum was really a precious metal, used chiefly for fancy articles. The price was in:

1855	\$90.00 a pound
1856	27.00 a pound
1857	22.50 a pound
1862	12.00 a pound
1886	12.00 a pound

\$12.00 a pound was the lowest price at which aluminum was sold during the work of Deville and his associates.

In 1869 I purchased a little basket in Paris at the aluminum salesroom for \$9.00. It weighs 125 grams—about one-quarter of a pound. That was the commercial position of aluminum as an every-day metal in 1869.

In 1886 Hamilton Y. Castner, one of our students in the School of Mines, invented a new process for making sodium. He employed caustic soda in place of the carbonate of soda, and iron carbide in place of carbon as a reducing agent. The result was he reduced the cost of sodium from one dollar per pound to twenty-five cents per pound, a very important item for the aluminum industry, as it was never possible to make a pound of aluminum with less than three pounds of sodium. By June, 1888, his works at Oldbury, near Birmingham, were in working order, with a daily output of 250 pounds of aluminum which he sold at that time at five dollars a pound. In 1889 a sufficient market had been created for aluminum to enable Castner to increase his output to 500 pounds daily at four dollars a pound. Then his manufacture of aluminum came to a sudden end because a new electrical process had been invented which produced it for one dollar a pound.

There had been created a company with a large amount of capital, and the stock had been widely distributed, a great deal of which, as is usual in such cases, was held by "widows and orphans." Castner felt he owed something to those holders of stock in his company, and he immediately devoted his energies to producing other products, and he made a large market for metallic sodium. He also produced metallic sodium electrolytically at low cost, to be used for the manufacture of cyanides and peroxide of sodium, and the enterprise remained a financial success.

We now come to the achievements of Charles M. Hall, but before I go any further I wish to say that whatever praise I shall bestow on this great inventor, I do not in the slightest degree disparage that other great inventor, Paul L. V. Héroult, whom we have the honor to have with us this evening who worked on the same problem, at the same time, across the Atlantic. He made the same discovery independently, and worked out an analogous process of manufacture, which has played the same important part in Europe that Hall's process has played in the United States.

Charles Martin Hall was born in Ohio, January 6, 1863, was educated in Oberlin, and graduated there in June, 1885, when twenty-one years and six months of age.

He studied chemistry while at school, became interested in the aluminum problem while in college, and made many experiments in the hope of finding a more economical process for its production. Finally his thoughts turned to electrolysis, and about the first of October, 1885, he began to seek a suitable anhydrous solvent for alumina, operative at a practicable temperature, which would bring the alumina into solution and which would yield to the electric current. That was the problem that Hall, almost as a boy, had set for himself.

Fluorspar, and the fluorides of magnesium, sodium potassium, and aluminum were successively tried, but were found to be too infusible, and to dissolve little, if any, alumina.

On February 10, 1886, Hall tried cryolite, the double fluoride of sodium and aluminum. This fused

readily at a moderate temperature, and when he dropped in the white powder of alumina it dissolved and disappeared as does powdered sugar or salt in boiling water. It dissolved to the extent of more than 25 per cent., and the solution was clear and limpid. You may imagine his delight when he saw the alumina dissolve. Why didn't Deville discover that when he used the cryolite as a flux?

It was well known that cryolite could be electrolyzed—Deville electrolyzed aluminum out of molten cryolite, but that was an impracticable process for the manufacture of metal.

Hall thus made his first great discovery. He proceeded at once to apply the electric current to this cryolite solution. His first experiments with clay crucibles were not successful, but on February 23, 1886, he employed a carbon-lined crucible and was successful in obtaining aluminum. He had achieved success in inventing a process for making aluminum directly from alumina by electrolysis under conditions which promised to revolutionize the industry and furnish the metal at so low a price as to enable it to replace copper, tin, lead, zinc and other metals for an endless variety of purposes.

I may say that our other guest to-night, Dr. Paul Héroult, and Hall are the same age, so there were two young men just out of college, one on the western side of the Atlantic, and the other on the eastern side of the Atlantic, making the same discovery, reducing it to practice, and devising a new process, at the same time, and at the same age—both boys, you might say.

Hall's age at this time was two months over 22 years and he had discovered and invented what had escaped Wöhler, Rose, Deville, and many of the other world-renowned chemists who had busied themselves with aluminum over a period of half a century. I might add that in the quarter of a century which has elapsed since the discoveries of Hall and Héroult no one has succeeded in bettering what they did.

On July 9, 1886, Hall applied for his broad basic patent which was granted April 2, 1889, No. 400,766; I think it would be interesting to you to hear some of the claims:

"1. As an improvement in the art of manufacturing aluminum, the herein described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum and a metal more electropositive than aluminum, and then passing an electric current through the fused mass, substantially as set forth.

"2. As an improvement in the art of manufacturing aluminum, the herein described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum and sodium, and then passing an electric current, by means of a carbonaceous anode, through the fused mass, substantially as set forth.

"3. As an improvement in the art of manufacturing aluminum, the herein described process, which consists in dissolving alumina in a fused bath composed of the fluorides of aluminum, sodium, and lithium,

and then passing an electric current, by means of a carbonaceous anode, through the fused mass, substantially as set forth."

That is the form in which Hall expressed his invention, and the form in which his patent was granted.

He also received four additional patents for modifications of his original process.

Hall did not escape the usual experience of the successful inventor. He was obliged to defend in court the originality of his invention. A suit was brought in the U. S. Circuit Court of the Northern District of Ohio, and after an exhaustive discussion of the prior art, the patent was sustained. The opinion was written by Judge William Howard Taft, now the President of the United States. He wrote: "Hall was a pioneer, and is entitled to the advantages which that fact gives him in the patent laws." The court declared the patent valid and issued a perpetual injunction against the defendants.

For various reasons there was considerable delay in devising suitable means for applying the invention on a manufacturing scale and securing the necessary capital. At last, in November, 1888, Hall began work in his factory at Kensington, near Pittsburgh, producing fifty pounds of metal a day. Since then his progress has been wonderful. He soon erected larger works at Niagara Falls, as the first consumer of the electricity supplied by the Niagara Falls Power Company. At the present time his company has three establishments at Niagara Falls—one at Massena in New York on the St. Lawrence, and one at Shawenigan Falls in Canada. The total consumption of electricity is 140,000 horse-power, which I believe to be a larger amount of electricity than is consumed by any other electrochemical works in the world. The annual output of aluminum is now *forty million pounds*.

The first metal produced at Kensington was sold on the market at two dollars per pound; the price now is about twenty-two cents—a slight drop from Deville's \$12.00 per pound. The early dreams of the young undergraduate have certainly been realized.

Hall has made many other inventions, several of which have been patented. Six of these are for improved methods for preparing pure alumina, one of which is still employed for preparing this material for use in his works. He has also patented methods for making improved carbon anodes for use in the process.

There are very many other matters in connection with Hall's work to which I should be glad to call your attention, did time permit. I think, however, that I have laid before you a most creditable record of discovery which will satisfy you that your committee has been wise and just in awarding to Dr. Hall the gold medal which was established to honor forever the memory of the great chemist, Sir William Henry Perkin, and by association with him to honor our own most distinguished fellow-chemists.

Dr. Hall's achievements certainly entitle him to a place in the front rank of electro-chemists, and his youthful successes must ever prove an encouragement

to other young men who develop a love for this branch of applied science. Personally, Dr. Hall is a man of the greatest modesty, and most lovable character.

(Addressing Mr. Hall) Charles Martin Hall, Doctor of Laws—My Dear Friend—It gives me the greatest pleasure as the representative of the affiliated Chemical and Electrochemical Societies, to place in your hands this beautiful token of appreciation and affection of your fellow-chemists. (Presents medal.)

REMARKS IN ACKNOWLEDGMENT BY MR. HALL. *Mr. Chairman, Ladies and Members of the Chemical Societies:*

I thank the speaker for his kind remarks and for the medal which he has given me, and for the great honor which it represents. And through him I thank the representatives of the chemical societies to whom I am indebted for this honor. I appreciate it the more highly because it is awarded by fellow-workers in the chemical and electrochemical profession and industries. I am glad to have this medal on account of what it represents and on account of the manner in which it has been given, and I shall treasure it among my most valued possessions.

It is an especial pleasure also, Mr. Chairman, to receive this medal and this honor from the hand of the distinguished Past-President of the Society of Chemical Industry, the Dean of the chemical profession in America—a man who has been my adviser, helper, and my friend for many years.

It has been suggested to me to give an account of some of the more personal and unpublished facts in connection with my invention of the aluminum process, and of the work of putting it on a commercial basis.

My first knowledge of chemistry was gained as a schoolboy at Oberlin, Ohio, from reading a book on chemistry which my father studied in college in the forties. I still have the book, published in 1841. It is minus the cover and the title-page, so I do not know the author. It may be interesting now to see what this book, published seventy years ago, says about aluminum: "The metal may be obtained by heating chloride of aluminum with potassium in a covered platinum or porcelain crucible and dissolving out the salt with water. As thus prepared it is a gray powder similar to platinum, but when rubbed in a mortar exhibits distinctly metallic lustre. It fuses at a higher temperature than cast-iron and in this state is a conductor of electricity but a non-conductor when cold."

Later I read about Deville's work in France, and found the statement that every clay bank was a mine of aluminum, and that the metal was as costly as silver. I soon after began to think of processes for making aluminum cheaply. I remember my first experiment was to try to reduce aluminum from clay by means of carbon at a high temperature. I made a mixture of clay with carbon and ignited it in a mixture of charcoal with chlorate of potassium. It is needless to say that no aluminum was produced. I thought of cheapening the chloride of aluminum

then used as the basis for aluminum manufacture, and tried to make it by heating chloride of calcium and chloride of magnesium with clay, following the analogy by which iron chloride is produced when common salt is thrown into a porcelain kiln. A little later I worked with pure alumina and tried to find some catalytic agent which would make it possible to reduce alumina with carbon at a high temperature. I tried mixtures of alumina and carbon with barium salts, with cryolite, and with carbonate of soda, hoping to get a double reaction by which the final result would be aluminum. I remember buying some metallic sodium and trying to reduce cryolite but obtained very poor results. I made some aluminum sulphide but found it very unpromising as a source of aluminum then, as it has been ever since.

On a later occasion I tried to electrolyze a solution of aluminum salt in water, but found nothing but a deposit of hydroxide on the negative electrode. I

rigged up a little electric battery—mostly borrowed from my professor of chemistry, Professor Jewett, of Oberlin College, where I had graduated the previous summer. I melted some cryolite in a clay crucible and dissolved alumina in it and passed an electric current through the molten mass for about two hours. When I poured out the melted mass I found no aluminum. It then occurred to me that the operation might be interfered with by impurities, principally silica, dissolved from the clay crucible. I next made a carbon crucible, enclosed it in a clay crucible, and repeated the experiment with better success. After passing the current for about two hours I poured out the material and found a number of small globules of aluminum. I was then quite sure that I had discovered the process that I was after.

I undertook to broaden and improve the method, and found that I could use, instead of cryolite, other double fluorides, particularly a double fluoride of



NEW PLANT OF ALUMINUM COMPANY OF AMERICA. NIAGARA FALLS.

did not give a great deal of time to these experiments, as I was then a student in college and was working on three or four other attempted inventions.

I had studied something of thermochemistry, and gradually the idea formed itself in my mind that if I could get a solution of alumina in something which contained no water, and in a solvent which was chemically more stable than the alumina, this would probably give a bath from which aluminum could be obtained by electrolysis.

In February, 1886, I began to experiment on this plan. The first thing in which I tried to dissolve alumina for electrolysis was fluorspar, but I found that its fusing point was too high. I next made some magnesium fluoride, but found this also to have a rather high fusing point. I then took some cryolite, and found that it melted easily and in the molten condition dissolved alumina in large proportions. I

potassium and aluminum. The most important change, however, which I made at this time, was in the material used as an anode. I wanted to get rid of the burning up of the carbon anodes. I tried a platinum anode and found that it seemed to work all right, but it was too expensive. I discovered that if I used a fusible bath of a potassium double fluoride with a sodium double fluoride, I could use a copper anode, which immediately became coated with a thin film of copper oxide and acted like a permanent platinum anode. This was not a step in advance as I had hoped, because more or less copper got into the reduced aluminum, and the use of a copper anode led me to use very fusible baths, which on the whole did not work as well as the less fusible baths. It is probable that this change delayed a successful result for a year or two.

When worked on a small scale, this process with

any of the baths I have mentioned, and with either copper or carbon anodes, is not apparently promising. The ampere efficiency is low, sometimes zero, and the bath, whether composed of sodium or potassium salt, becomes filled with a black substance which accumulates and renders the process very difficult. I presume that my friend, Dr. Héroult, whom I have the pleasure of seeing here to-night, who invented the process independently in France about the same time, encountered the same difficulties. In spite of the difficulties mentioned, however, I had great faith in the theoretical possibilities of the process, and believed that the practical obstacles could be overcome, so I stuck to it from the start.

On the financial side I had, in the course of three years, three different sets of partners or backers, of whom two sets became discouraged and gave up. In the summer and fall of 1886, I worked with some people in Boston with whom my brother had made some financial arrangement. The results there obtained were not satisfactory to them and in October, 1886, my Boston friends declined to go further.

In December, 1886, I returned to my home in Oberlin, continued my study, and found that a bath composed of a very fusible double fluoride of aluminum and potassium, with copper anodes, worked much better than anything I had before tried. I have here a number of buttons of aluminum made by this method at that time. The larger one was made with current from a galvanic battery on December 7, 1886, and weighs about 8 grams.

After this I negotiated with the head of one of the large chemical manufacturing companies of the United States with headquarters at Cleveland, but we could not finally agree. I thought then, and have thought since, that this gentleman was the kind of man whom the proverbial inventor meets when he is deprived of the fruits of his labor. He was described to me as extremely careful and conservative, and was always wanting to take a few days more to think the matter over. He kept me on the string six months, and the kind of contract which he finally offered seemed to me entirely one-sided. The gentleman told a friend of mine afterwards that I was no business man (which was no doubt true), but I received what seemed to me much fairer treatment from all with whom I afterwards had business dealings, and found much more liberal associates and friends.

The Cowles Electric Smelting & Aluminum Company, who were then making aluminum alloys at Lockport, N. Y., were the second set of people who became interested in my invention. They took an option on it, and I spent a year with them, from July, 1887, to July, 1888. They finally gave up their option. The baths which I used at Lockport worked well for a few days, but after a time became less efficient. I finally worked out a system by which the difficulties were overcome. This was by making a bath consisting partly of calcium fluoride, or fluorspar, and adding 3 or 4 per cent. of calcium chloride, and using carbon anodes. I reasoned that chlorine was evolved and burned up the objectionable compound

which spoiled the bath. After finally overcoming the difficulties which I have mentioned, I made several pounds of aluminum in small crucibles, which I showed to Mr. Alfred Cowles and gave him all the facts in relation to the same, but he was not interested.

I then sent a representative—Mr. Romaine Cole, now dead—to Pittsburgh, to get together the gentlemen who formed the Pittsburgh Reduction Company, now the Aluminium Company of America. We started in in the summer of 1888 to build and operate a commercial plant on Smallman Street in Pittsburgh. We had at our disposal about fifty horse-power in electrical current of 2,000 amperes. It took a few weeks after starting to get the dimensions of our baths just right, and then the difficulties which I have referred to disappeared as if by magic. The clogging and spoiling of the bath, which had caused trouble for the last three years, did not occur on a large scale. No calcium chloride was required. It seems that this is a process (unlike a good many others) which works badly on a small scale and well on a large scale. I accounted for this by the fact that on a large scale the electrodes are further separated and there is less circulation between the positive and negative electrodes, which lowers the efficiency and favors the formation of the clogging black compound. We also found, as I had predicted nearly three years before and had stated in a patent application filed two years before, that on a commercial scale no external heat was required to keep our baths in fusion. This was a great advantage, but I believe that it resulted from a law of nature and not from any invention, as we did not use any excess of current for maintaining fusion, but only the normal current and voltage for electrolytic purposes. The use of the electric current for fusing and heating in connection with electrolysis was a thing which had been disclosed and published almost a century before.

The manufacturing of aluminum has now grown to a great commercial business. Many workers have contributed to it, and the credit is to be divided among many. Our financial people, particularly the gentlemen of the Mellon Bank, of Pittsburgh, have given indispensable aid. Our patent attorneys and experts, our engineering and chemical staff, sales-agents, superintendents, foremen and others have all done their share. In the commercial development of the business I think the greatest credit is due to our first President, Captain Alfred E. Hunt, who died in 1899, and to our present President, Mr. Arthur V. Davis, who has been identified with the business for twenty-two years, and who has been manager and general of our forces for the last eleven years.

THE CHAIRMAN: I am sure that our best wishes go out to Dr. Hall, and that all hope that he may possess the medal with honor and pleasure for many years, and that it will bring him all kinds of luck.

The electric smelting of aluminum and the applications of the electric arc and the electric furnace to the reduction and refining of metals are in all probability the greatest technical problems, and of the greatest

importance to the world of any of the great problems on which scientists are working to-day.

It is fortunate that the men who have done the pioneering are men of great concentration and great resource, men who have a grim determination about them and let nothing interfere with the attaining of success.

Such a man is the gentleman I am about to introduce, who, in a generous spirit and with devotion to the science, has consented to add to-night to our fund of knowledge about aluminum. I have the honor to introduce to you Paul L. V. Héroult.

MR. PAUL L. V. HEROULT: There is a verse of Kipling which reads as follows:

"Ship me somewhere East of Suez,
Where the best is like the worst;
And there ain't no ten commandments,
And a man can raise a thirst."

I was in that particular mood when I made my first acquaintance with aluminum in large quantities. At the time I had a friend who since then became my partner, but for the time being we were both "dead broke." We had pawned everything in sight and also other things which were not in sight. Finally my partner had a bright idea. He brought from home a stick of aluminum about six inches long, which was valued very highly by his family as a personal souvenir of Sainte Claire Deville. As we handed it to the pawnbroker, the latter said: "What is that—bar silver?"

We said: "Better than that, that is aluminum." "Aluminum," he said, "What is that?"

He weighed it in his hand and said: "Why! is that hollow?"

We said: "No, that is aluminum and it is worth 120 francs per kilo."

After some thought he said: "Well, I will give you two francs for it."

On a hot summer's day it was better than nothing and we took the money with the firm intention of buying the stick back, which we never did.

Maybe that was one of the reasons why, later on, I had to make good and replace it.

No material change took place in the industry of aluminum for three years after that event, but the development of the industry was preceded by rumors to the effect that something new was coming.

I can remember there was a shop on the Grand Boulevard in Paris, where there was a display of aluminum goods, mostly thimbles, if I remember rightly, besides wedding rings, brooches, statuettes, a few coils of wire and some interesting specimens of aluminum bronze in the form of coffee pots, sugar bowls, etc. I once bought a thimble for my mother out of my savings—I was a good boy in those days. Every one of those articles had on the Paris finish and sold like silverware.

In the nineties, this same shop maintained the same prices, although the cost for ingots had fallen as low as 25 francs per kilo. This was a wonderful time for the aluminum dealers and they were making money hand over fist—at least on the books.

There was no use for any syndicate at that time. Aluminum was being piled up in the store and the stock of finished product reckoned at above-named price, but this did not last long; customers were scarce and finally the bankers got tired of lending money to people who piled up stock, it became necessary to sell. Another price was established at eight francs per kilo, which also did not prove successful.

Then came a price of five marks which originated with the Swiss Company and it seemed to open the bung-hole of the cask. Now, after various vicissitudes, the price in the Old Country looks pretty near settled around twenty cents per pound and will vary according to the price of copper.

Twenty-five years ago the aluminum industry employed about ten men: the production was one and a half tons a year, the total value of which was 150,000 francs. Now the same industry produces 50,000 tons per year at a value of one hundred million francs or twenty million dollars, and employs from fifteen to twenty thousand men. If we take the average consumption of copper at 900,000 tons a year at a value of thirteen cents per pound, the total value of ingot copper will be two hundred and thirty-four million dollars a year compared with twenty million dollars for aluminum.

But thirteen cents is pretty near the rock-bottom price for copper. At twenty cents per pound aluminum presents a great advantage for most uses. It is slowly wedging its way into the metal market. It looks probable that in a course of ten to fifteen years the consumption of the new metal will be equal to that of copper, and that after the golden age, the stone age, the bronze age, and the iron age, we will have the aluminum age.

My friend Hall and myself have been fighting for fifteen years, most of the shots going wild on account of the long range over the Atlantic Ocean. Since we met, however, we conceived a better opinion of each other, and I take great pleasure to-night in extending to my friend Hall my sincere congratulations on the award to him of the Perkin medal.

THE CHAIRMAN: Dr. Héroult had added a new page to the history of aluminum, and has given us some of the human aspects of the question.

We have in our company to-night a man who is an authority on aluminum, and a delightful gentleman whom we are always glad to see with us—Professor Richards, of Lehigh University.

PROF. RICHARDS: I think this is an historical occasion. In the whole history of aluminum, which has extended nearly a century, from the time of Wöhler, there has been no occasion on which aluminum has been so prominent, and so praised, and has stood forth as it does to-night. With this exhibit here as a backing for me, one cannot but think of the past struggles which metallurgists and chemists have gone through to bring this industry to what it is to-day.

In 1827 they were barely making a little gray powder. For nearly thirty years in the chemical museums, that represented the world's supply of aluminum. Deville made such a small quantity

that he could not sell it for less than ten dollars a pound. Then we come to Castner who made it on a large commercial scale, and brought the price down to one dollar a pound. He wrote me a pathetic letter in 1889 saying "that the price of aluminum has reached one dollar a pound, we will have to go out of business." Then, we had the invention of Mr. Hall.

It was in 1885 that my father was using aluminum in the metallurgy of zinc, and was buying some of it from Germany at six dollars a pound. Later he bought still more, and he wanted to get a lower price. He asked me to look up the history of it, and to give him the information. In 1887, I had sufficient information gathered to publish a little book on the subject. It was in that year I first made the acquaintance of Mr. Hall. I am going to claim a part of this triumvirate of ages: Mr. Hall, Mr. Héroult, and myself are within one year of each other. I remember when I first met Mr. Hall. I looked at him and he looked at me. I had expected to find a middle-aged man, and he expected, as I learned afterwards, that I was a gray-bearded university professor. We found out later that he was twenty-four years of age and I was a little over twenty-three.

Now, there are a few things about Mr. Hall's experience, in which I am going to supplement Dr. Chandler's remarks. Mr. Hall was a classical student, and not a scientific student in college, and I believe his classical training has given him the broad views necessary for his scientific success. I wish every technical man could have a classical education to start with.

I cannot help thinking of the course from the woodshed to the Perkin medal. When Mr. Hall made his first experiments in Oberlin, and wanted a battery to run the electric current through the electrolyte he chopped the wood and he cast with his own hands the zinc-plates for his galvanic battery. From that time on it has been grim determination and hard work, and he richly deserves all he has received.

Dr. Chandler has asked me, with these samples as an inspiration, to say something about the present uses of aluminum. Aluminum, when my father was buying it at six dollars a pound, was used for telescopes and articles of luxury. At the present time the list of articles is so great it would be impossible to read it in less than an hour.

One of the chief uses of aluminum is in the manufacture of steel. There is hardly a steel works in all the world where aluminum is not used to solidify the steel castings. A Swedish inventor showed that a little homeopathic pill of aluminum weighing perhaps one ounce to the ton of metal, put in as the metal is poured, solidified the steel by removing the gases, which make the castings unsound. I do not know what the steel-maker would do without it.

Another use is for electrical conductors. It is giving copper a hard race. It may not be known to all of you that a conductor one mile long, of a given carrying capacity, is cheaper with aluminum than with copper. Aluminum, section for section, is not quite as good a conductor as copper, but make the

section 25 per cent. larger in diameter, and that gives you 50 per cent. larger area, with much more satisfactory results. The weight gives it certain advantages over copper, for one-half a pound of aluminum takes the place of one pound of copper and does the same electrical work. There are other advantages, as well as a few disadvantages, which I cannot go into now, but thousands of tons of aluminum are now being used, for long distance transmission lines.

There is a large use of aluminum in the reduction of the other rare metals. It has such a great affinity for oxygen that it will reduce the oxides very easily and cheaply.

Our friend Hans Goldschmidt used it in his process, which he called aluminothermy. Here is a large piece of chromium metal produced by this process; tungsten, vanadium, molybdenum and others are produced comparatively cheaply by this method.

An adaptation of the Goldschmidt process, which is very wonderful, is that for welding. If a mixture of aluminum powder and iron oxide is made and ignited, it burns violently, and forms aluminum oxide, plus iron, and the heat generated is so great that the iron is liquefied, and at a temperature far above the melting point. The melted iron can be poured on the ends of two rails and will weld them together—the Goldschmidt thermo-welding process. In several cases a broken shaft of a steamship has been welded at sea by this process, and now all of the German warships and German merchant marine vessels must carry it with them in order to repair shafts in case they break.

Another extensive use is for culinary utensils. It interests not only the ladies, but all of us. There is no doubt this is the ideal metal for cooking utensils. The ware, if sufficiently thick, is practically indestructible, it cannot be worn out. I have in my own home some of the first aluminum vessels, stamped in 1892; they have been used constantly since that time, and apparently they will not wear out in our lifetime. That use of aluminum is increasing rapidly. When you consider its durability, it is the cheapest ware you can use. I think that is to be the largest use of aluminum. Hundreds of thousands of tons will be consumed for that purpose when its virtues are known.

Stiffening aluminum for construction of bodies for automobiles and castings around the motors—in fact, any construction that must be light and at the same time strong is of great importance. We hear monthly, almost, of new alloys of this character. There is one in Europe which reliable reports say has a tensile strength nearly equal to that of soft steel, and with a specific gravity of aluminum. When those alloys come into general use, I think there will be large uses for that metal in flying machines.

Most of you are familiar with the aluminum paint which is used on radiators and open plumbing, etc. But why should I try to catalogue all of those things? Most of them are familiar to all of you.

I think we can look forward to the continued extension of the aluminum industry. The aluminum has become a commercial metal. If you want to make an

object out of metal, there are only three metals which you can use, which would be cheaper than aluminum—iron, lead, and zinc.

In conclusion, I regard the bringing of aluminum—into the rank of the cheaper metals, as one of the great metallurgical achievements of the 19th century, and I think the historian of the future will probably class the industrial manufacture of aluminum alongside the invention of Bessemer steel. The man who takes a rare metal, and makes out of it a common metal, and brings it into every-day use, has made the entire human race his debtor.

THE CHAIRMAN: One of the societies invited to suggest names for the candidates for this medal is the American Electrochemical Society, and are fortunate in having with us to-night the President, Dr. William H. Walker.

DR. WALKER: I have enjoyed taking part in these proceedings, and on behalf of the members of the American Electrochemical Society, I want to endorse the action of the committee in presenting this medal to Mr. Hall. The history of this invention sounds like a story from Fairyland. On behalf of our society, I congratulate Mr. Hall, and wish for him many, many long years of life in which to enjoy the honor and distinction.

THE CHAIRMAN: Dr. Baskerville representing the American Chemical Society, New York Section.

DR. BASKERVILLE: *Gentlemen:* The American Chemical Society takes great pleasure when any fraction of it is honored; consequently the members have been looking forward to this honor which he so well deserves coming to Mr. Hall.

I think the committee has done itself honor in giving the medal to Mr. Hall for his great discoveries.

THE CHAIRMAN: Dr. Takiama, Director of the Japanese Agricultural Department, is in this country studying technical chemistry in its commercial applications, and is our guest this evening.

DR. TAKIAMA: I wish to congratulate, in the name of my countrymen, the great discoverer, Mr. Hall.

THE CHAIRMAN: Now, gentlemen, the meeting will be adjourned in order that you may have an opportunity to extend your personal congratulations to Mr. Hall.

ORIGINAL PAPERS.

THE SPONTANEOUS COMBUSTION OF COAL.

By S. W. PARR AND F. W. KRESSMAN.

Any examination into the causes underlying the spontaneous combustion of coal resolves itself, naturally, into a study of the various forms of oxidation to which such material is subject. It involves the determination not only of the conditions which permit of such action, but also those which promote or accelerate it, as well as the interrelation of the various oxidation activities upon each other. Studies have been carried on for some time in the Department of Chemistry, in coöperation with the University of Illinois Engineering Experiment Station, which have resulted on the whole in a considerable amount of data bearing upon the topic. For example, in the

studies connected with the weathering of coal, there was found to be a drop in fuel values which occurred with marked uniformity in the first few days after the breaking out of the coal from the mine. An illustration of this fact is shown in the accompanying chart, which is typical of all of the samples in that a rapid drop in values is indicated for the first ten days or two weeks of the experiment.

These studies which were published as Bulletin 38 of the University of Illinois Engineering Experiment Station, while they afforded a partial explanation for this drop in values in the fact of a loss of hydrocarbons, mainly methane, gave evidence also of an additional factor in the avidity of the freshly-mined coal for oxygen. This phase of the matter was further taken up by Perry Barker, and the results published in Bulletin 32, entitled "The Occluded Gases in Coal." These experiments afforded abundant confirmation of the fact that freshly-mined coal very rapidly absorbs oxygen and in a manner which does not result in the formation of carbon dioxide, but by direct incorporation into the molecular structure to satisfy certain of the unsaturated compounds. Such absorption must, therefore, be looked upon as a type of oxidation of the coal. A table of results is here given which is typical of the many obtained in this study in which there is evidence of the fact that the freshly-mined coal, especially in the form of drillings taken at the face of the vein and sealed in a glass vessel, will rob the enclosed air of its oxygen even to a fraction of a per cent.

TABLE I.—AVIDITY OF OLD AND FRESH COAL FOR OXYGEN.

- I. Atmosphere surrounding old face sample in contact with large volume of air for 2 years.
- II. Old face sample sealed in fresh air 2 days, then evacuated.
- III. Drillings, sealed 14 days.
- IV. Drillings, in vacuum 12 days.
- V. Drillings, second air in contact with coal 7 days.

	I.	II.	III.	IV.	V.
Weight of coal, grams.....	146	205.5	220	220	220
Volume of gas, cc.....	843	33.5	192.1	48.8	130.4
Per cent. by volume.					
CO ₂	0.25	7.80	3.86	7.58	1.63
O.....	0.25	15.50	1.04	0.61	0.37
CH ₄	2.17	0	21.79	86.37	14.14
N.....	97.33	76.70	73.31	5.44	83.86

In this table all samples were from the same mine. No. I and No. II were partially air-dried face samples, which had been sealed in Putnam jars for some two years. From No. I, the surrounding air in the container was collected by displacement and analyzed. No. II was left in one of the sealed fractionating flasks for two days. At the end of that time both the surrounding air and some of the enclosed gases were removed by means of the air pump. No. III is a flask of fresh drillings from which the surrounding air and occluded gases were removed by vacuum, as above. No. IV is the analysis of the further gas given off after the surrounding air had been removed and the flask had stood in a vacuum for twelve days. No. V is the analysis of the air that had been readmitted to the evacuated flask and left in contact with the coal for seven days. This is a type of many similar results obtained in this work which give evidence not only of the marked

avidity of freshly-mined coal for oxygen, but also of the fact that the product of oxidation is not carbon

thermometer, T, is inserted for the purpose of giving the temperature of the surrounding gas. Now upon the application of heat externally to the flask F, and taking a log of the temperatures upon thermometers, T and T', at the same time continuing the circulation of the gas through the chamber, an indication may be had of the effect of chemical activity upon the temperature of the coal mass. A train of wash bottles is introduced to purify the air from all traces of carbon dioxide, so that a test may be obtained of the first appearance of carbon dioxide in the discharged gases by means of barium hydroxide solution.

A few of the charts are here appended in which is given a log of the thermometer readings. It is seen that there is a first appearance of carbon dioxide in all cases at a point slightly above 120° C. This activity on the part of the coal does not seem to reach a point where its heat exceeds that of the surrounding air until a somewhat higher temperature is reached, 140° to 160° C. At this higher temperature two phenomena are observed: a much more evident appearance of carbon dioxide in the discharged gases and a rise in temperature on the part of the coal which carries the thermometer readings ahead of those for the surrounding atmosphere in the flask. In all the charts an additional item of interest is to be noted; namely, that at a certain point the rise in temperature becomes very rapid.

In Fig. 3, with Pittsburg gas coal in an atmosphere of oxygen, this rapid rise begins at 175° and quickly reaches the point of combustion, which is made evident by the appearance of fire.

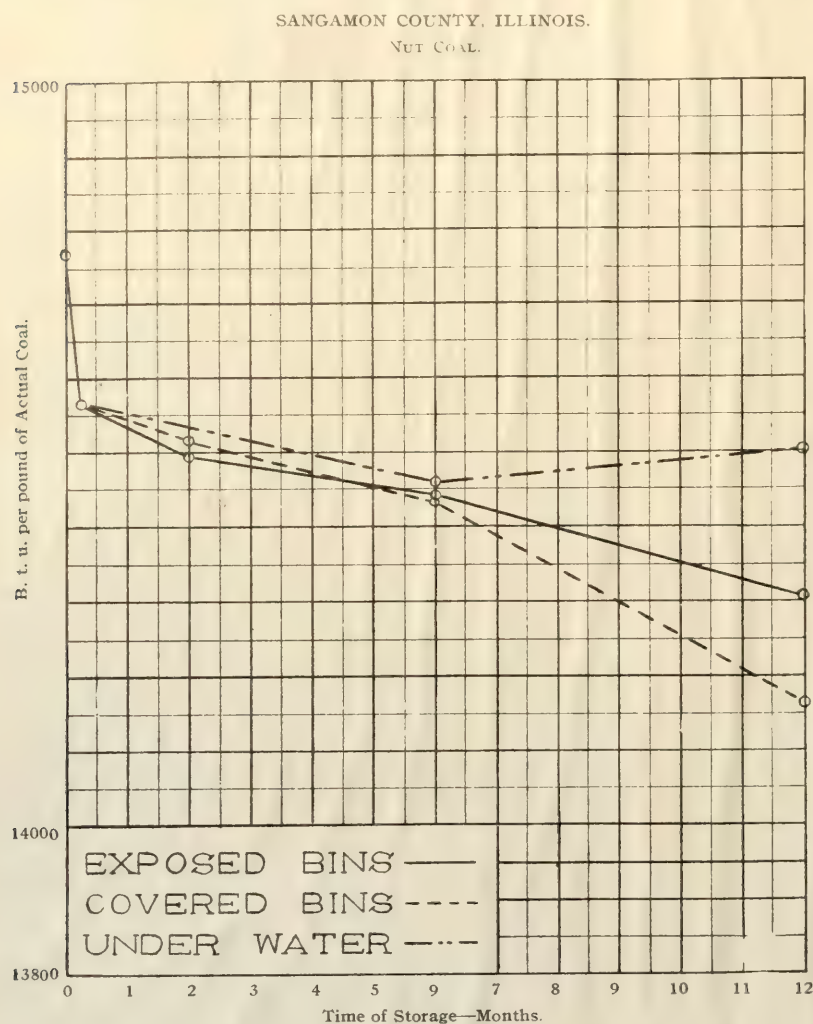
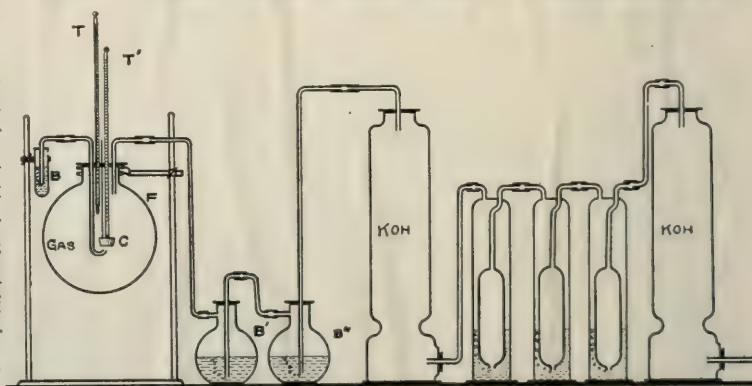


Fig. 1.

dioxide, or at most to only a limited extent. These results were substantially the same also as those obtained by Chamberlain¹ in a similar line of research.

A third study in which there was obtained much incidental data on oxidation was carried on by Mr. C. K. Francis and published under the title of "The Modification of Illinois Coal by Low Temperature Distillation." This work was published as Bulletin 24 of the University of Illinois Engineering Experiment Station. In these studies there was obtained much interesting data upon the oxidation of coals at temperatures above 120° . In order to understand the full import of that study, it is necessary to reproduce the apparatus in which these experiments were carried out.

The large globe F is arranged with an inlet and an outlet for the circulation of a gas, while two thermometers, T and T', are inserted, one for indicating the change of the temperature of coal contained within the capsule C, while the other



OXIDATION OF COAL
AND
TEMPERATURE MEASUREMENTS

Fig. 2.

In Fig. 4, this rapid rise begins at 240° , the coal being an anthracite.

In Fig. 5, the coal is of the Illinois type and in

¹ United States Geological Survey, Bulletin No. 383.

an atmosphere of air. Here the rapid rise is more or less in evidence after 210° has been passed. In this latter chart a further observation is made at a temperature of 210° where the external source of heat was withdrawn, whereupon the activity within the coal ceased and there was an indication that the temperature would fall to that of the surrounding gas. However, upon a reapplication of the heat, the oxidizing condition continued until a point was reached at 285° where the removal of the external source of heat was without effect in so far as a cessation of oxidation was concerned. We have evidence, therefore, that oxidation of carbon with formation of carbon dioxide begins at about $125-135^{\circ}$, and that an autogenous stage is reached at about 280° .

Further experiments were next taken up as hereinafter described¹ with a view to a more definite determination, not only of the fundamental causes of oxidation, but the relative importance of the various phases involved, including especially the influence of iron pyrites which numerous foreign investigators have pronounced of little or no concern in the matter.²

The apparatus is illustrated in Fig. 6 and is explained as follows: A large box with dimensions $3' \times 3' \times 3'$ had within it a second box of smaller dimensions, approximately $2\frac{1}{3}' \times 2\frac{1}{3}' \times 2\frac{1}{3}'$, thus affording about 4" of space upon all sides. This space was filled with mineral wool as an insulating medium. Within the inner box was then placed an earthenware jar capable of holding from 35-40 pounds of coal and having $\frac{1}{8}"$ perforations in the bottom to facilitate the circulation of air. Across one corner of the inner chamber a board 7" wide was fastened in such a manner as to enclose a triangular space about $5" \times 5" \times 7"$, and extending from near the bottom to near the top of the chamber. A chimney was thus formed for both heating and circulating the air. It was lined with asbestos and fitted with a number of electric lights. These were operated by a relay controlled by a mercury column which would cut the lights out at a given temperature. In this manner the air surrounding the coal mass was maintained at a fixed temperature. Thermometers were inserted, one in the air space about the jar and the other penetrating the coal mass. An indication of temperatures from both thermometers was thus obtained, the readings being taken twice daily for three days. Four such ovens were arranged in order to introduce the variable

of temperature, the first oven being carried at 40° , the second at 60° , the third at 80° and the fourth at approximately 115° . Aside from external temperature, the other variables which were introduced were those of size of particles, the content of sulphur and the effect of moisture. In the matter of size three divisions were made use of. The first or O size was pulverized by a disc machine to such an extent that all of the coal would pass through an 80-mesh sieve. Other sizes were prepared by crushing the coarse coal in a jaw crusher and passing the material through a revolving screen. The second division or size $6-1\frac{1}{8}"$ included all the material passing the $\frac{1}{8}"$ holes.

PITTSBURG GAS COAL-POWDERED ATMOSPHERE OF OXYGEN

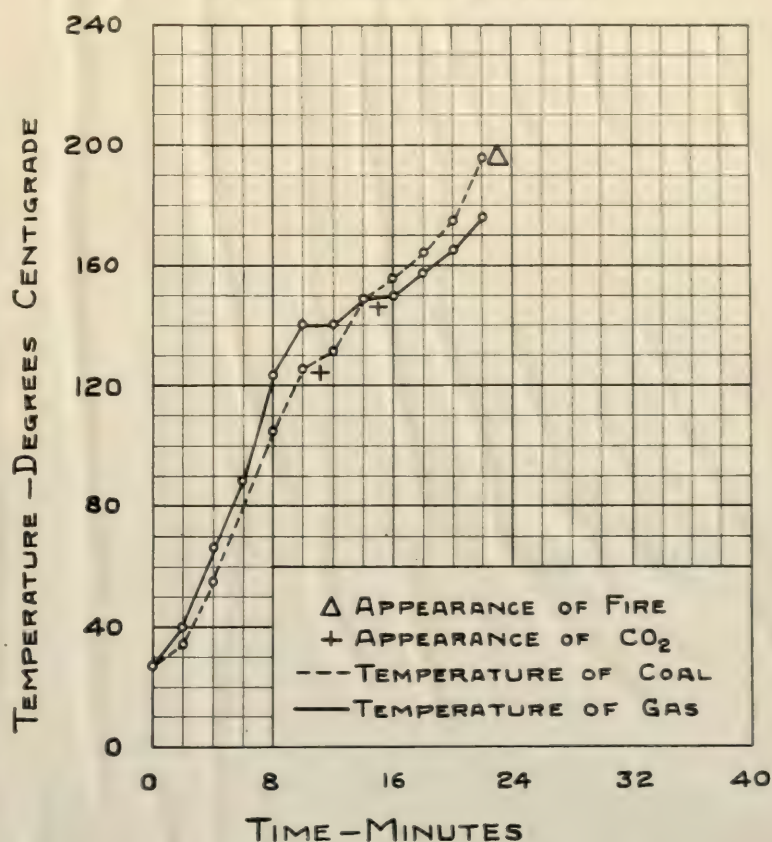


Fig. 3.

The third division or size $\frac{1}{8}-\frac{1}{4}$ was made up of such coal as would pass over the $\frac{1}{8}"$ and through the $\frac{1}{4}"$ perforations. Coarser sizes were used in a few of the preliminary experiments, but the results were not essentially different from the third division already described and they were consequently dropped out of the series. In order to indicate at a glance the results obtained the charting of a few of the logs is presented herewith as follows:

In Fig. 7 there is shown the activity of oxidation for each size and also as influenced by the variations in temperature, the greatest rise over the oven temperature being shown by the finer coal and in the higher oven. This order of variation is consistent throughout the series where the two variations are

¹ To be printed in full in *Bulletin*, No. 47, of the University of Illinois Engineering Experiment Station.

² Richter, *Dingler's Poly. J.*, **190**, 398; **195**, 315, 449; **193**, 54, 264. *Lewes, Journ. Gas Lighting*, **55**, 645, also **1906**, 33. Fayol, *Bulletin de la Société de l'Industrie Minérale*, **8**, [2] Part 3, 1879. *Report of the First New South Wales Commission*, inquiring into the causes of the firing of coal cargoes, etc.

those of size and temperature. In the course of the first experiments the exhaustion of the oxygen of the chamber was made evident so that a method of changing the air was introduced, thereby securing uniform conditions as to the supply of oxygen.

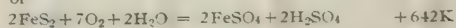
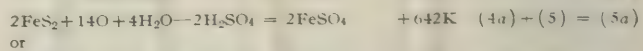
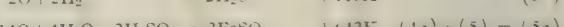
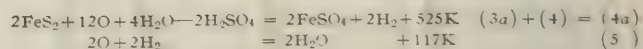
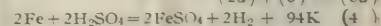
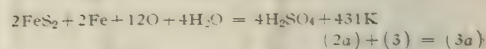
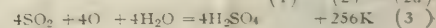
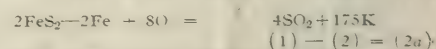
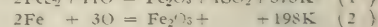
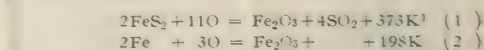
The next variable which was introduced was that of moisture, wherein the sample of coal was thoroughly saturated with all the water it could hold, being simply drained free from the excess of water. The effect of this variable upon both the size and temperature

content, wherein the conditions were otherwise the same.

In the next test, Fig. 10, the variable of moisture was introduced and a consistently higher indication of temperatures was shown throughout. It is interesting to note that the rise in temperature begins soon after 80° has been reached instead of waiting until a total volatilization of the water at the boiling point had been attained. Here in the 0 and 0-1/8" sizes the condition of autogenous oxidation was reached and the coal continued its activity after being removed from the last oven until reduced to ash. A thin zone of unburned coal, however, remained around the sides and over the top of the jar where the cooling effect had brought the material down below the ignition temperature.

Identical results are obtained in the next two succeeding tests, Figs. 11 and 12, where the amount of pyrites was brought up to 5 per cent., showing a thoroughly consistent behavior throughout in regard to the four fundamental items; namely, external temperature, fineness of division, sulphur content and moisture. In the last test, with the introduction of water, sizes 0 and 0-1/8" (see Fig. 11) continued their oxidation activity after removal from the oven until all of the interior was reduced to ash.

In connection with the oxidation of iron pyrites, an extended examination of the residual product was made to determine the actual amount of oxidation which had taken place in connection with the iron sulphide. In all cases the total amount of oxidation of this material in the period of time, 12 days, in which each sample was under observation very closely approximated 20 per cent. of the total sulphur present. The amount of heat generated by transferring this amount of FeS₂ to FeS₄ is calculated as follows:



It will thus be seen that the total volume of heat discharged would equal 642 Calories per gram molecule (2 mols.). No account is made in this calculation of the heat of solution of the sulphuric acid nor of the hydration of the ferrous sulphate. If we assume the weight of a jar of coal as being 40 pounds (18.12

1 "K" is used to represent the large Calorie.

ANTHRACITE - POWDERED ATMOSPHERE OF OXYGEN

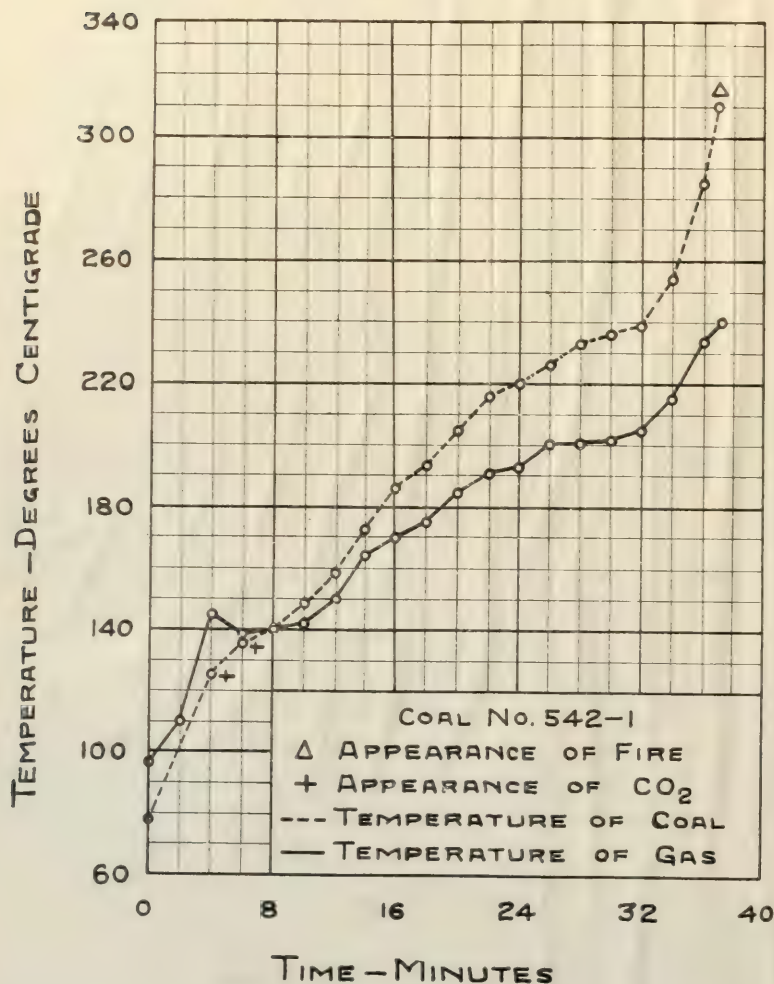


Fig. 4.

conditions is shown in Fig. 8, wherein a consistent rise slightly above the temperature increase as indicated in Fig. 7 is shown throughout.

In Fig. 9 there is introduced the variable of iron pyrites. The amount of iron pyrites, FeS₂, in the first two series was 1.65 per cent. In the second series this was increased to 3 per cent. by the addition of sufficient material ground to pass a 20-mesh sieve to bring the percentage up to the equivalent of 3 per cent. pure FeS₂. The first test with this modification was carried through upon the dry samples with a very vident rise in temperature over the lower sulphur

kilograms), and if the coal contains 5 per cent. of coal. If we assume the specific heat of the coal used pyrite, then it will contain 2 pounds (906 grams) of to be 0.35,¹ then the heat generated by the oxidation pyrite. The latter is 19.3 per cent. oxidized, then of the pyrite would be sufficient to raise the tempera-

BITUMINOUS COAL-POWDERED

ATMOSPHERE OF AIR

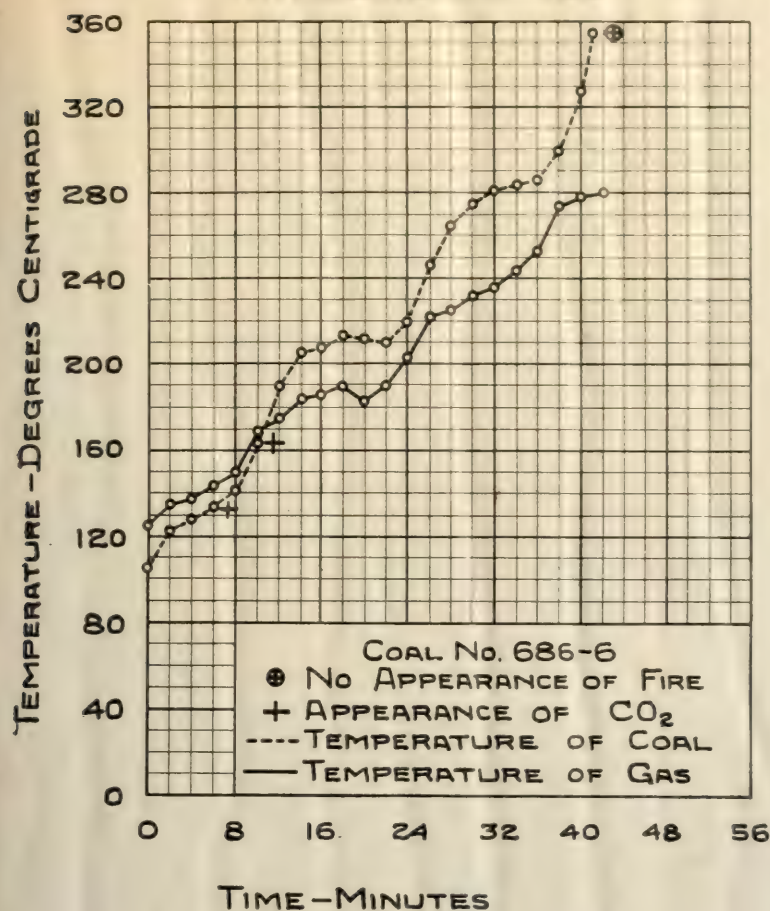


Fig. 5.

19.3 per cent. of 906 grams will enter into the reaction, or 177 grams. The molecular weight of pyrite is 120, and two molecules entering into the reaction would be 240, so we will have $\frac{177}{240} \times 642$ K or 473 K as the heat liberated by the oxidized pyrite in 40 pounds of

ture of the coal $\frac{473}{18.1 \times 0.35}$ or 74.5°

which it is seen is sufficient in amount to account for the larger part of the increase as indicated by the curves. This fact has a very direct bearing upon the conclusions arrived at and must be considered directly contradictory to the results obtained by those foreign investigators who have declared the influence of sulphur to be inoperative or too small in amount to bear any part in the matter of spontaneous combustion.

A very considerable number of experiments were carried out intended to determine the effect of various possible deterrents, such as the saturation of the coal with a strong salt brine, solutions of ferrous sulphate, sodium bicarbonate, etc. A saturated solution of lime water and a 10 per cent. solution of NaHCO₃ were about equally effective in preventing a rise of more than 45° above the oven temperature. Under corresponding conditions, *i. e.*, with 5 per cent. pyrites in size 0-1/8" in the 115° oven, the increase over the oven temperature was over 100°, making a total of 220°, which was well up to the point of autogenous oxidation. While the coal as treated with the alkaline solutions, under like conditions, only reached a temperature of 165° and still below the autogenous stage, there does not seem to have been a sufficient check to chemical action to warrant the conclusion that such treatment would be of practical value. It is, however,

suggestive and warrants further experiment along that line.

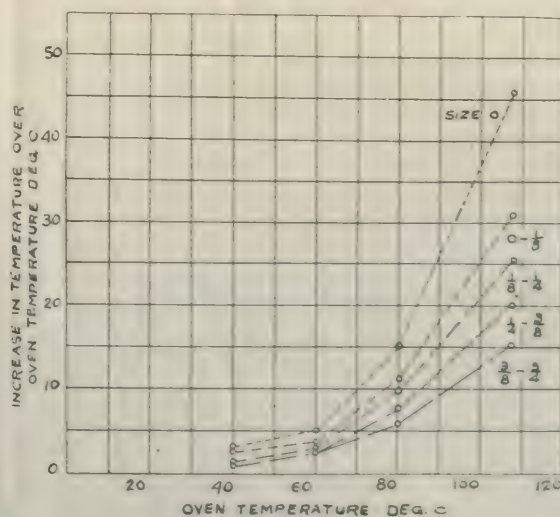


Fig. 7



Fig. 6

Other experiments looking to remedial measures were tried, such as a seasoning or artificial oxidation

temperature approaching the point of autogenous action, that is, to somewhere near 200°C . They were then cooled down to ordinary temperature and

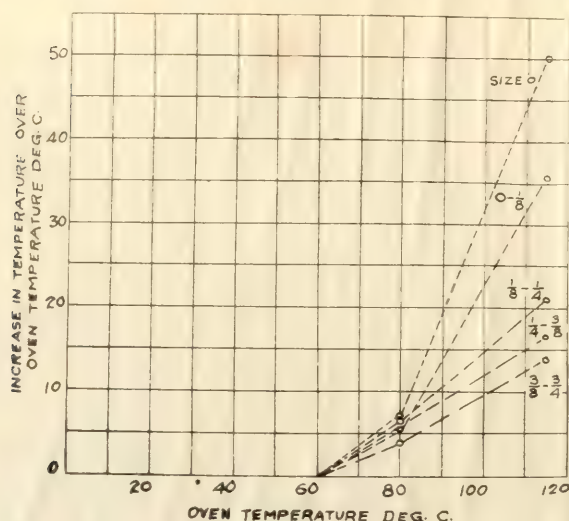


Fig. 8.

by a process of preheating. Three sizes were used, A being a mixture of coal passing a $1/4$ " screen, B

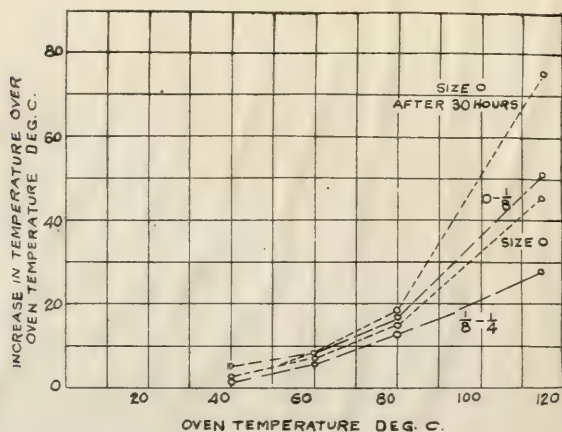


Fig. 9.

being the usual $0-1/8$ " size and C being coal ground to an impalpable powder in the ball mill. Each size was placed in an oven and the mass brought to a

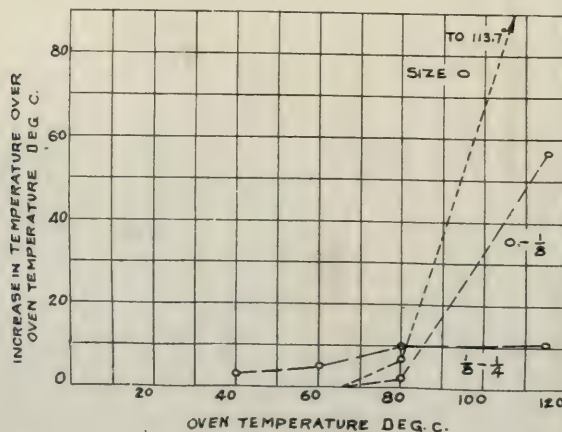


Fig. 10.

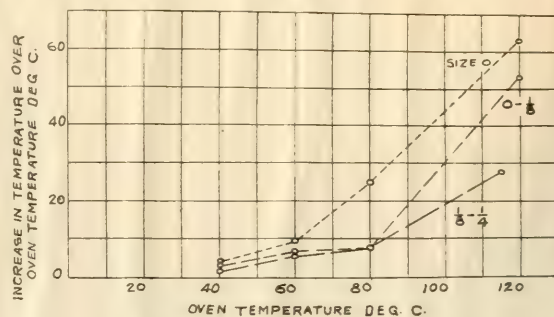


Fig. 11.

returned to their respective ovens which were maintained for three days at the same temperature as before. The increase for the first heating and that for

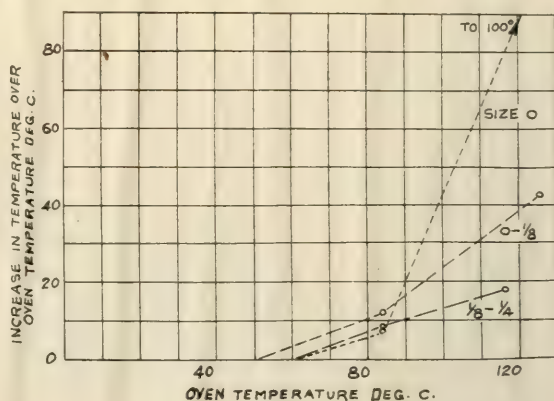


Fig. 12.

the second are joined by dotted lines in Fig. 13, which shows at a glance the marked difference in oxidation activities in the treated coal.

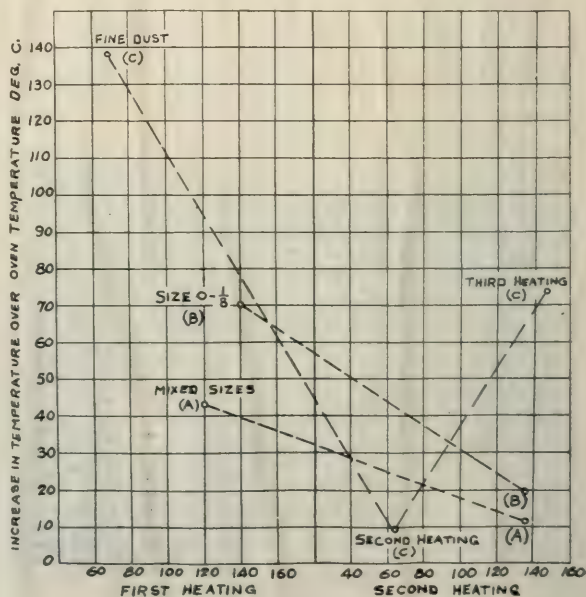


Fig. 13.

CONCLUSIONS.

From this brief résumé of oxidation conditions, the conclusions arrived at are as follows:

1. The oxidation of coal is continuous over a wide range of time and conditions, and begins with the freshly-mined coal at ordinary temperatures. A number of oxidation processes are involved which are more or less distinct in character, some being relatively slow and moderate in form, while others are rapid and vigorous in their action.

2. In general, we may say that for a given coal a point exists as indicated by the temperature, below which oxidation is not ultimately destructive and its continuance is dependent upon certain accessory conditions which, if withdrawn, the oxidation ceases. On the other hand, above this critical point, which is best indicated by temperatures, oxidation is ultimately destructive and is characterized by the fact that it does not depend for its continuance upon external conditions, but is self-propelling or autogenous.

3. The point of autogenous oxidation, while varying for different conditions, may be indicated by temperatures of the mass ranging from 200–275° C., depending to a great extent upon the fineness of division. The phenomenon of fire or actual kindling does not occur until a much higher temperature is reached, usually beyond 350° C.

4. The temperature at which autogenous oxidation begins is the sum of numerous temperature components, each one of which, either because of its own contribution to the total heat quantity or because of its function as a booster for chemical activities, must be looked upon as a dangerous factor tending directly to the ultimate result of active combustion throughout the mass. An enumeration of the more important elements which contribute towards this end are the following:

A. External Sources of Heat.—Oxidation, especially of the lower or moderate form, is greatly accelerated and in certain phases directly dependent upon an increase of temperature. What may be termed external or physical sources of heat, and thus presumably avoidable, are suggested by the following:

(1) Contact of the mass with steam pipes, hot walls or floors under which are placed heat conduits of any sort.

(2) The heat of impact or pressure due to the method of unloading or to the depth of piling.

(3) Climatic or seasonal temperature at the time of storage.

(4) The direct absorption of heat from the sun or from reflecting surfaces.

B. Fineness of Division.—Coal in a fine state of division presents a very much larger surface and brings a much larger quantity of reacting substances in contact with oxygen than when in solid masses. Under these conditions, with a condensation or accumulation of relatively large amounts of oxygen immediately surrounding or in contact with the particles of carbonaceous matter, the circumstances are exceedingly favorable for rapid oxidation upon the arrival of the mass to a suitable temperature.

But, more especially does this fineness of division facilitate the initial form of oxidation described under C below.

C. Easily Oxidizable Compounds.—A first or initial stage of oxidation exists in bituminous coals which does not result in the formation of carbon dioxide. There are present in coals of this type unsaturated compounds which have a marked avidity for oxygen at ordinary temperatures, the products being humic acid or other fixed constituents of the coal texture. Coals vary widely in this matter and it has been proposed by some to regard this property as an index of the liability to spontaneous combustion. It is, however, very largely dependent upon the freshness of the coal and upon the fineness of division (see under B above), and should be looked upon as a contributing factor, though in coals of the Illinois type at least, with their high per cent. of sulphur, this action should doubtless be considered second in importance to that of iron pyrites.

D. Iron Pyrites.—The presence of sulphur in the form of iron pyrites is a positive source of heat due to the reaction between sulphur and oxygen. This may be conveniently referred to as the second stage in the process of oxidation. Here again rapidity of oxidation is directly dependent upon fineness of division. Since coals of the midcontinental field especially have a much higher earthy or ash content in the fine material, and since iron pyrites is a large component of this substance, it follows that the presence of dust or duff in all coals of the Illinois type is a positive source of danger. Since coals of the Illinois or midcontinental field have in the large number of cases iron pyrites averaging over 5 per cent. or as sulphur above 2½ per cent., the heat increment from the oxidation of only ⅓ of this material is sufficient to raise the temperature of the mass approximately 70°, assuming that there is no loss by radiation. Under usual conditions and especially considering the greatly accelerated rate of chemical activity accompanying a rise of temperature, this oxidation may proceed with such rapidity that the heating up of the mass will be but little affected by loss of heat due to radiation, except in relatively shallow piles. Coals of low sulphur content or such as do not have sulphur greatly in excess of, say, 1½ per cent. are popularly supposed to be immune from heating, but no method of selection or hand-picking at the mine can eliminate all of the iron pyrites. Lumps of coal, to all outward appearance of good texture, may have nodules or bands of iron pyrites. These become centers of activity and with the addition of moisture such coal will have many detached spots where heating begins. If fine coal is mixed in with the coarse, the difficulty is accentuated. Doubtless a complete separation of fine and lump material in such cases would lessen the danger.

E. Moisture.—Moisture, while essential to pyritic oxidation, is given separate mention because its importance is apt to be underestimated. Any coal with pyritic conditions as above mentioned will be facilitated in that action by moisture. It is to be noted in this

connection that the normal water content or vein moisture of coals in this central region is rarely below 10 per cent. and ranges usually from 12-15 per cent. The presence of such water must be borne in mind in considering the likelihood of chemical activity on the part of the pyrites present.

F. The Oxidation of Carbon and Hydrogen.—A third stage of oxidation of the carbonaceous material exists by reason of the property of certain of the hydrocarbon compounds of coal to oxidize with the formation of CO_2 and H_2O at temperatures in excess of $120-140^\circ$. Though this type of oxidation does not take place appreciably at ordinary temperatures, it must be looked upon as an exceedingly dangerous stage in the process of oxidation, owing to the very much higher quantity of heat which is discharged by the oxidation of carbon and hydrogen; so that the temperature of autogenous action, though ordinarily occurring at a higher point by 100° or more, may be quickly attained as a result of this form of oxidation. Any initial heat increments, therefore, which threaten to bring the chemical activities along to the point where the oxidation processes invade the carbonaceous material in this manner must be looked upon as dangerous. For example, any of the initial or contributory processes which result in raising the temperature of the mass 50° above the ordinary temperature would, in all probability, have enough material of the sort involved in such action to continue the activity until another 50° had been added, which would thereby attain to the condition wherein this third stage of oxidation would begin.

G. The fourth stage of oxidation may be indicated as occurring at temperatures above $200-275^\circ$ and differs from the previous stages in that the action is autogenous and not dependent upon other sources of heat to keep up the reacting temperature. Activity in this stage is further accelerated by the fact that above 300° the decomposition of the coal begins, which is exothermic in character, thereby contributing somewhat to a further increase in temperature. The ignition temperature is reached at a point still further along, usually in excess of $300-400^\circ \text{C}$.

The above formulation of the various stages and types of oxidation clearly indicate the principles which must be observed in any attempt at the prevention of spontaneous combustion. The following enumeration, therefore, of preventive or precautionary measures is to be considered as suggestive rather than complete in character.

First, the avoidance of external sources of heat which may in any way contribute toward increasing the temperature of the mass is a first and prime essential.

Second, there must be an elimination of coal dust or finely-divided material. This will reduce to a minimum the initial oxidation processes of both the carbonaceous matter and the iron pyrites. These lower forms of oxidation are to be looked upon as boosters, without which it would be impossible for the more active and destructive activities to become operative.

Third, dryness in storage and a continuation of the dry state, together with an absence of finely-divided material, would practically eliminate the oxidation of the iron pyrites. The drenching down with water of heating piles, where the sulphur content is high and uniformly distributed, accentuates the difficulty. Where pyritic activity is localized in spots or is so small in amount as to reach a possible exhaustion, the drenching with water may check the heating or prolong the action so that oxidation of the carbonaceous matter does not get under way to a serious extent. In such cases, however, there is no ultimate safety except in the removal of the heated zones.

Fourth, artificial treatment with specific chemicals or solutions intended to act as deterrents does not offer great encouragement, though some results seem to warrant further trial in this direction.

Fifth, by means of a preliminary heating the low or initial stages of oxidation are effected. These sources of contributory heat being removed the forms of destructive oxidation are without the essential of a high starting temperature and are, therefore, inoperative. Whether such preliminary treatment is within the realm of practical or industrial possibility could not, of course, be determined within the scope of these experiments.

Sixth, the submerging of coal, it is very evident, will eliminate all of the elements which contribute towards the initial temperatures. As to its industrial practicability, like the conditions under 5 above, it can best be determined by actual experience.

Other processes may be suggested by the formulation of the principles involved. Such, for example, would be the distribution throughout the coal of cooling pipes through which a liquid would circulate having a lower temperature than the mass. This would serve to carry away any accumulation of heat and confine the oxidation to the lower stages only. On the contrary, the proposition sometimes made to provide circulating passages for the transmission of air currents is of questionable value, since it may result in the contribution of more heat by the added accessibility of oxygen than will be carried away by the movement of the air.

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THE CENTENARY OF GLUCOSE AND THE EARLY HISTORY OF STARCH.

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The year 1911 is the centenary of the discovery of the inversion of starch to glucose by means of dilute acids. During these hundred years, glucose has become one of the most important products of chemical manufacture, an importance which is only emphasized by the very close relation of glucose to agriculture. It is the simplest and best known representative of that great group of substances known as carbohydrates, which form the body structure of all vegetable growth, and the main sustenance of animal life, a fact in itself sufficient to give glucose a most prominent place in chemistry.

To attempt to review the history of this discovery at this time seems, therefore, not only excusable, but also pertinent, and to do this with any degree of success, the early history of starch—the mother substance of glucose—has to be included in order to preserve the historical connection.

STARCH BEFORE THE NINETEENTH CENTURY.

Starch—*amylum* made without milling—was known to the ancients. Its preparation from grain by a process of partial fermentation is described in the first book ever published on agriculture,¹ but the knowledge of this preparation must have antedated this publication by many centuries. It is stated that 800 years before Christ, starch was used for stiffening new fabrics, but its application in laundering was introduced in England at the time of Queen Elizabeth, who made it a source of state revenue.² The Egyptians used starch in cosmetics and probably also in medicines, for which purposes it was employed extensively in subsequent centuries. The name "Kraft soup" or "Stark soup" was given to the decoctions prepared with starch, and probably had as much to do with the modern term "starch"—"Staerke" as did its application for strengthening fabrics.

Both Plinius and Dioscorides³ mention starch, saying that the best came from Crete and Egypt, where it was made from grain by the addition of fermenting matter, using sieves, and quick-drying on porous stones (bricks) to prevent souring. The Jatrochemists naturally made extensive use of it in the preparation of salves and internal medicines. Stahl and his great contemporary, Boerhave, seemed to have formed some conception as to the part starch plays in the fermentation of the grains, but the first scientist who is on record as having submitted starch to a closer investigation was Leuwenhoek,⁴ the traveling Dutch microscopist, who as early as 1716 gave enlarged reproductions and detailed description of the structure of the starch grain as he saw it through his magnifying glass. In 1749, Beccari, an Italian physician, made known his observations on flours which he summarized in the statement that they are composed of gluten and starch (*fecula*)⁵ and this seems to be the first record of an investigation of a chemical nature, to which starch containing materials had been subjected, although Macquer in his *Dictionnaire de Chimie*, published in 1773, states that the possible separation of flour into gluten and starch was known before Beccari. From that time on, investigations relating to starch became more frequent and although they mostly were undertaken from some utilitarian point of view and in connection with cereal foodstuffs generally, they yet contributed largely to a more intimate knowledge of the chemical nature of starch. Macquer quotes also at the same

place the work of Kessel Meyer, who wrote about the nourishing principle of some plants in 1759, and Rouelle, who in 1770 gave analyses of grain in *Journal de Medicine*, and Fourcroy¹ adds the names of many other chemists—especially Parmentier—who were engaged in the chemical investigation of flours and starch. Lavoisier mentions starch casually in his researches on fermentation, and the subject of starch is also treated in the investigations on pollens made by Luke Howard (1795). Some of the observations made during these researches, though sporadic and unconnected, were yet of a quite striking character and would have anticipated far-reaching discoveries if the then general status of our science would have permitted them to be pursued in a systematic and effective way.

At the beginning of the 19th century but one thing was positively known of starch regarding, what we have now come to call, its cleavage products—namely, that during the process of malting it is changed in part into a sugary substance which is capable of subsequent alcoholic and acetic fermentation.

During the 18th century we find also that attempts were made to get at some source of starch other than grain, which was then very expensive, too much so to be used as a raw material for a product which was becoming more and more a necessity.

In 1736² a sieur de Guife presented a petition to the French parliament asking to be permitted to make starch from potatoes. The petition was turned over to the Academy for investigation which later (1739) reported recommending that the request be granted, saying that though the paste made from starch is thicker, yet it is not as applicable for many purposes as that made from grain starch, but that the grain had better be reserved for food purposes.

The same problem evidently was encountered also in other countries, for we find that in 1796, wheat having become very dear in England, the Society for the Encouragement of Arts offered a prize of thirty guineas, or a gold medal, to any person who would indicate another source than grain from which to make starch. In 1797, the Society voted to give the prize of thirty guineas to Mrs. Jane Gibbs, of Portland, who in a communication to the Society, notarially attested, stated that she had made 200 pounds of starch from the roots of *arum maculatum* (arrow root), extracting about four pounds of starch from a peck of roots. She sent a description of the process and included a sample of the starch.³ If not the first, this surely is one of the earliest instances of woman trying her skill at chemical inventions, although in this instance the invention was not entirely original, a sieur de Vaudreuil having already in 1716 recommended the use of this root for starch-making,⁴ a fact most likely unknown to Mrs. Gibbs.

The same year (1797) saw also the issue of a patent

¹ A. F. Fourcroy, *Elements d'histoire naturelle et de chimie*. Vol. IV. 176. Paris. 1782.

² *Histoire de l'Académie des sciences*. 1739, 24.

³ *Bulletin of the Society for the Encouragement of Arts*. Vol. 15, 237 (1797).

⁴ Diderot, *Encyclopédie methodique*. Paris. 1791.

¹ Marcus Porcius Cato, senior, *De agricultura* 184 B. C.

² L. Darmstadter, *Handbuch z. Gesch. der Naturwissenschaften*. Berlin. 1908.

³ Kopp, *Geschichte der Chemie*, Vol. IV, 406.

⁴ Leuwenhoek, *Epistolae physiol.*, Vol. IV, 230. Delphis. 1719.

⁵ The French differentiated later between "fécule," starch made from roots, and "amidon," starch made from grain.

to Lord Murray for extracting starch from horse chestnuts.¹ There is no inconsiderable irony of fate in the fact that the invention of Mrs. Gibbs has proved of more practical value than that of the noble Lord.

Up to within modern industrial times the making of starch was in the hands of a strong guild, subject to repeated regulations on the part of the civil authorities. The starch being made by souring away the gluten, the vicinity of a starch factory was by no means a pleasant abode for working men or neighbors, and regulations to abate the nuisance were frequent. In 1806 the Société pour l'encouragement des Arts at Paris offered a prize for a method to make starch other than by fermentation, but it was years later before such a method was devised.

The knowledge of sugars and gums did certainly not go beyond that of starch, the only differentiation known was the formation or nonformation of mucic or oxalic acid, the ability or inability to sustain alcoholic fermentation and some few other minor reactions. Yet in spite of this meagre knowledge the intimate chemical connection of these substances with one another and with starch was almost intuitively guessed and formed part of the then scientific creed not only of the chemists, but of scientists generally. Furcroy² held that the sugar pre-exists in the starch, that it contains less carbon than gum arabic, and thus seems to hold the middle place between the two, and that the transition of starch into sugar is possible by a peculiar alteration of its substance. Lippman, in his history of sugar, reprints an interview held before 1800 between Napoleon and the great astronomer Laplace, in which the latter is made to say:

"There are three substances which have the same basic principle; namely, gum (arabic), starch and sugar. They differ only under certain conditions, the nature of which has remained a secret as yet." The interest of Napoleon in these matters was, of course, of an entirely practical nature and manifested itself later in a more direct way in the embargo which he put on all products coming from England and its dependencies.

DEXTRIN.

It was toward the middle of the first decade of the 19th century that starch experienced its first important chemical development, when (1804), as we are led to surmise, Bouillon Lagrange first observed the change which starch undergoes when submitted to high temperatures. The starch thus treated changed outwardly but little except in color and became entirely soluble in water forming a viscous solution resembling that of gum. The name dextrin was given it only more than 20 years later by Biot. Whether it was the commercial importance of the discovery or otherwise we do not know, but the fact is that the first notice of it which crept into

literature in 1811³ created no little interest among men of science and of commerce. It led eventually to a discovery of far greater importance.

Seldom, if ever, was an invention made at a more psychological moment than that of the conversion of starch into sugar by means of dilute acids.

It is well to remember that at the time we speak of, *i. e.*, around 1810, Europe was one seething cauldron of war. Financially and economically all Europe was on the verge of ruin, some parts even beyond the point. In 1803 Napoleon had established an embargo against all products of England and its colonies. Some of the most important necessities of life were forbidden entrance, sugar among them. Napoleon gave all the support possible to the development of the beet sugar industry, but the progress was slow. After Proust had (1803) established that a sugary substance (grape sugar) could be extracted from the juice of the grape,⁴ he was offered, by Napoleon, a large sum of money to try his scheme on a manufacturing scale. A commission was appointed to report on this invention and in 1810, the report being favorable, an imperial decree was issued that beginning with January 1, 1811, all public institutions of France were to use this new sugar instead of cane sugar.⁵

DISCOVERY OF GLUCOSE.

Colonial sugar, or cane sugar, was almost unobtainable on the continent except at fabulous prices. Yet the demand for it was great and insistent. The scarcity and high price of honey prevented its being used as a substitute to any extent. On the other hand, in England, the stock of sugar had accumulated in an alarming ratio, and could not be disposed of at any price except as a food for cattle.⁶ With other articles that had to be imported from or through England and the colonies the case was just as bad. One of these articles was gum arabic, which was used very extensively for many purposes in spite of its high price, being practically the only gum then commercially accessible. A young German chemist by the name of Kirchhof, an "adjunct" in chemistry at the Academy of Science of St. Petersburg, Russia, apparently was then engaged on some work in connection with the manufacture of porcelain by the new process invented by Boettcher for which he required

¹ *Bulletin de Pharm.*, **3**, 54, 216 and 395 (1811). While it was, incontestably Vaucquelin, who in 1811 in a casual way first described the formation of dextrin from starch by torrefaction and gave the properties of the substance so formed, indicating its commercial possibilities, yet it cannot be denied that Bouillon Lagrange knew of the reaction before and utilized it in making a substitute for gum arabic to be used for fixing dyes and making ink. In *Ann. de Chim. et de phys.*, **50** (1804), he speaks of having prepared such a substance without however giving the directions, but did so immediately after Vaucquelin had published his observation.

² *Journal de Physique*, **56** (1803).

³ *Bull. de la soc. pour l'Encouragement des Arts*, **9**, 160 (1810).

⁴ Lippmann, *Geschichte des Zuckers*, Leipzig, 1890. Lippmann writes in his history of sugar, page 424, that during the continental blockade, smuggled sugar cost in France up to 6 francs per pound (\$1.20), in Germany very little less, while in England there was accumulated a stock of sugar and coffee to the value of 15,000,000 pounds sterling, and sugar went begging at 34 shillings per cwt. (about 8 cents per pound).

¹ Tillocks, *Philosophical Magazine*, **7** (1797).

² Quoted by Vogel in *Annales de Chimie et de Physique*, **82**, 148 (1812).

gum arabic. Unable to obtain this, he tried to use the substitute made from starch as described in the experiments made by Bouillon Lagrange and Vauquelin, which had just been published. In the course of its preparation, Kirchhof tried to achieve the same results in another way, perhaps with the intention of getting clearer solutions and of avoiding discoloration, due to the high temperature and in some way or other was led to subject a suspension of starch in water to the action of sulphuric acid. He must have continued his treatment for too long a time, for after he had neutralized his acid, filtered off the gypsum and evaporated the solution so obtained, he noticed that he had made a sweetish syrup instead of a gummy one.

Kirchhof's first observation with regard to the conversion of starch by diluted sulphuric acid must have been made very early in 1811, as it is only natural to assume that he would have repeated the experiment several times, in order not only to satisfy himself, that no error had slipped into his observations and deductions, but also to ascertain the best conditions under which the reaction takes place. Peculiarly enough no account of the invention seems to be outstanding, written by the inventor himself, unless it be in the inaccessible proceedings of the Petersburg Academy. From descriptions and accounts given by others, and which will be referred to later, it can be seen that Kirchhof made known the results of his experiments at once to his immediate chief, Prof. Nasse, who represented the chemical science in the Petersburg Academy, and he in turn, in appreciation of their scientific and more so of their economic importance under the then prevailing conditions, communicated it to the authorities.

A governmental commission was appointed to investigate the matter and under its supervision the experiment was repeated. The sugar so prepared was highly satisfactory, equally so must have been the report of the commission for it is stated that the Russian Emperor offered a prize of ten thousand rubles to the first man who would prepare 40 puds,¹ equal to about 1600 pounds, of the sugar by the method devised by Kirchhof. The only recognition which the inventor seems to have received in an official way was his admission as a full-fledged member of the Petersburg Academy of Science, with the material emoluments going with it.

The first public intimation which the outside scientific world received of Kirchhof's invention is contained in a communication of Prof. Wm. Nasse to the celebrated physicist Brugnatelli, who published it at once in his *Journal*.² Nasse, who was a corresponding member of several scientific societies and correspondent to several scientific journals, wrote of the discovery to some of them, and this explains that the few publications then existing on the continent relating to the science of physics and chemistry

published accounts of it almost simultaneously in the first half of the year 1812.¹

The method of preparing the sugar as given by Kirchhof through Nasse was to use 100 parts of starch, 400 parts of water, and 1 part of sulphuric acid. It was recommended to dilute the acid with half the quantity of water and bring to a boil. The starch was made into a milk with the rest of the water and poured gradually into the boiling acid mixture which was kept stirred and at boiling temperature for 36 hours in succession in open vessels, renewing occasionally the water lost by evaporation. Neutralization with calcium carbonate, followed by filtration over bone-black and evaporation of the sugary liquid to a syrupy consistency, finished the operations. The syrup left for a certain time began to crystallize—usually about the third day—and was separated from the mother liquor through filter bags and pressing.

From 100 parts of starch Kirchhof obtained 90 parts of solid sugar or 120 parts of very sweet syrup.

The sugar is described as less sweet than cane sugar, with a peculiar after-taste which, however, can be removed by refining. The diminished sweetness is caused, in the author's opinion, by the larger percentage of water of crystallization which can not be removed at higher temperature. The sugar resembles more the one obtained from grapes but is better than the latter.

In his letter describing the invention of Kirchhof, Professor Nasse stated that nitric, hydrochloric and oxalic acids act like sulphuric acid, transforming the starch into sugar, but not so acetic, tartaric and phosphoric acids. The sulphuric acid acts on the starch in the way indicated in all proportions, but when the quantity of the acid becomes too great then the solution must be diluted accordingly, and much care exercised in boiling, otherwise the sweetness of the sugar and the ability of the syrup to crystallize will be influenced adversely. It was also observed that at first a gummy substance is formed, and only on continuing the boiling sugar is obtained.

Kirchhof and Nasse had also tried hard to make the sugar directly from the grain without previous separation of the starch, but were not successful, even after they had submitted the grain previously to feeble fermentation. They only obtained in this way a slightly sweetish syrup in which, after twenty-four hours, alcoholic fermentation had set in.

CONTEMPORARY COMMENT.

Simultaneously with Nasse's letter in the *Journal de Physique* appeared a paper on the subject by the then well-known chemical authority, Vogel, of Paris.² Vogel had seen the letter before its publication, had repeated the experiments and made some relevant observations in connection therewith, of which the following deserve to be noticed here:

1. The gummy material formed simultaneously with the sugar, when sulphuric acid acts upon starch,

¹ Quoted by Lampadius, *Bull. Soc. d'encour.*, 11, 213 (1812).

² *Giornale di fisica di Brugnatelli Decada seconda*, Pavia, 1812.

¹ For other communications see: *Annales de Chimie et de Phys.*; *Bull. de Pharmacie*; *Schweigger's Journal*; *Journal de Physique*, all of 1812.

² *Journal de Physique*, 74, 200 (1812).

is separable by treating the syrup with alcohol of 85 per cent. strength.

2. Sugar and gum form in variable proportions, their total quantity being equal in weight to that of the starch used.

3. The syrup contains no sulphuric acid when properly purified.

4. The sugar is a true sugar as it maintains alcoholic fermentation.

5. Heat alone is not sufficient to transform starch into sugar.

6. Sugar of milk, treated with acid in like manner as starch, forms a syrup more sweet than the original sugar, and capable of fermentation.

A scientific discovery of this character would have attracted the utmost attention even under ordinary circumstances among the scientists of those days, and under the exceptional political and economic conditions then prevailing, to which attention was called above, the reception given it was little short of sensational.

The scientific periodicals of 1812, and even later, are full of accounts relating to the saccharification of starch by the method of Kirchhof. Authors from different parts of the continent, especially France and Germany, give their experiences and observations, made while duplicating the original experiments, and from casual remarks made in these reports it can be seen that it was not only the scientific world which was thus agitated, but that the excitement, which must have been general, was equally voiced with insistence in political circles and in the world of "belles lettres." The following may be considered as a fair example.

An account of the invention contained in the highly respected and widely read literary journal of that time, the "*Jenaische Literaturzeitung*," closes with the following flowery panegyric: "All hail to our wheatfields. In the future they will give us not only flour and starch, but will also satisfy one of our most refined needs—sugar."¹

INDUSTRIAL APPLICATION.

This discovery is exceptional also from another point of view, inasmuch as it was put to practical use almost immediately after its first publication, a fate not shared by many chemical inventions. The reasons for this are to be found in the peculiarly encouraging circumstances detailed above, under which it was made, and which caused that the manufacture of the starch sugar on a large scale was taken up immediately on many sides, unhampered by any patent restrictions which at that time had not yet been introduced. Scientists, technical and professional men, bakers and confectioners partook in this movement, giving later freely of their experiences.²

The first in line seems to have been the well-known chemist, Doeberiner, who in a letter to the editor of *Schweigger's Journal*, dated April 25, 1812, says that in view of the increasing demand made upon

him and others for starch-sugar and syrup, he had decided to erect a factory where these products would be manufactured and incidentally several improvements of a technical nature made by himself be utilized. The letter contains also another statement worth mentioning, which perhaps throws some light on the improvements meant, namely, that in his opinion starch can be saccharified by water alone if the time of boiling were sufficiently prolonged and the operations were carried out in a Papin digester (*i. e.*, under pressure).

Lampadius,³ of whom more later, states that the sulphuric acid manufacturers of Saxony cannot supply the increased demand for the acid, owing to Kirchhof's discovery, and that new works had been started.

Equally busy from a practical point of view they seem to have been in France and the *Bulletin de la Societe d'encouragement*, 11 (1812), contains three communications regarding the manufacture of starch sugar.

GLUCOSE IN ENGLAND.

The enthusiasm which filled continental Europe and the high hopes derived from Kirchhof's discovery, both of which, as we have seen, were due in large part to the peculiar economic and political condition of the times, were not shared in England for reasons readily understood.

Europe, through the tyranny of Napoleon, deprived of sugar for which there was no available substitute in spite of the hotbed cultivation of the young beet sugar industry, hailed with joy the prospect of obtaining a sweetener from starch, which its own wheat fields and potato crops supplied plentifully. England, on the other hand, was threatened by financial ruin, partly because it was overstocked with sugar which could not be disposed of while its grain supply was scant.

English scientists learned of Kirchhof's discovery only in the middle of 1812, and only during a visit of Berzelius at London,² who made personal communication of it to some members of the Royal Society. Their interest was of a more scientific character, though they did not entirely overlook the danger with which it threatened English commerce. The first mention of it is contained in Thomson's "*Annals of Philosophy*," where the editor says after describing the method of preparing the sugar:

"This curious process promises to throw additional light on the constitution of vegetable substances. In point of economy very little is gained, starch is in reality dearer than common sugar. Hence, even supposing starch sugar possessed the requisite qualities, it never could come in competition with common sugar, far less supplant it. At present it would be a much more valuable discovery in this country to convert sugar into starch than starch into sugar."

On the whole, however, English scientists paid so little attention to the subject that there seems not to be a single piece of experimental work on their

¹ Quoted in *Schweigger's Journal*, 4, 306 (1812).

² *Ibid.*, 4, 304 (1812); and also *Bull. Soc. d'enc.*, 1812.

³ *Bull. de Pharm.*, 4, 551 (1812).

² Thomson's "*Annals of Philosophy*," 1, 65 (1813).

part outstanding relating to it, which is remarkable in view of the fact that Englishmen had previously contributed largely to the knowledge of flours, starches and sugars, and were, then as now, as is well known, past masters in the art of chemical experimentation.

Within less than two years, Kirchhof, who now had found in starch a fruitful field of investigation, was able to communicate another important observation relating thereto, namely, that starch is transformed into sugar by gluten, especially from germinated seed, and that the gluten acquires this saccharifying quality by the germination.¹ This discovery, which gives the first experimental intimation of both maltose and diastase, remained fruitless to the author for many years. That he thought this sugar identical with the one produced by sulphuric acid is not to be wondered. In fact, as late as 1876² it was denied that maltose was a distinct sugar different from all others.

PRIORITY DISPUTED.

We are accustomed in these days to see practically every idea, which for some reason or other seems to assume a predominating importance, questioned and scrutinized as to its originality, and this not only by men whose motives might be suspected, but by also unbiased, competent authorities backed by arguments commanding attention. This is not surprising when we consider the almost inexhaustible store of accumulated observations of previous investigators which are hoarded in the archives of science, results of decades of intensive and extensive work. Kirchhof's discovery of the conversion of starch by acids, however, was made at a time when chemistry had barely begun to assert itself within the domain of recognized sciences, when the list of its accomplishments was rather restricted in number though imposing in quality and could therefore be readily overlooked. Yet this did not, as we shall see presently, prevent the question of priority from being raised.

The first contestants in the field was Lampadius, professor of chemistry and metallurgy in Freiburg, Saxony,³ who claimed the credit of the invention for himself almost immediately after Kirchhof's process had become known. What lends strength to this claim is the fact that Lampadius certainly was one of the best chemists which Germany then possessed, who bent his abilities more to technical purposes, ingenious, versatile, and many-sided, seeking at all times new fields of investigation and not afraid to go beyond the limits of theories and hypotheses whenever they seemed to conflict with or impede the progress of his work. He had been working for years on sugar and had also tried assiduously to find new uses for potato flour or starch. In his paper

¹ *Schweigger's Journal*, 14, 389 (1815).

² *C. R.*, 1876.

³ *Bull. de pharm.*, loc. cit. Among other things, Lampadius has studied the nature of the nitrous gases, experimented with central coal gas lighting, invented boiling and evaporating with steam under pressure, was one of the first to prepare beet sugar in loafs, discovered carbon-bisulphid, superintended the erection of sulphuric acid plants, sought to make soda ash from calcium acetate and sodium sulphate and igniting the sodium acetate formed, made barium carbonate from barytes by ignition followed by treatment with ammonium carbonate, etc., etc.

he calls attention to a pamphlet published by him some time before in which he is supposed to have given intimation of the conversion of starch into sugar, by means of the wooden vessels and steam coil evaporation invented by him.

But what, perhaps, may be considered as the strongest, though indirect support for his claim, is the fact that in the paper mentioned above is also found a full description of the process as used by him, with minute details as regards technical operation, use of materials, etc., down to a very valuable cost estimate of the process.

It seems not improbable therefore that Lampadius should have come very near the process before it was given to the public by Kirchhof, although F. Gehlen⁴, in his report to the Munich Academy of Science concerning the discovery, does not recognize his claim to priority.

The other contestant for Kirchhof's laurels was the Frenchman, Chevalier de Gassicourt, "Pharmacist to the Emperor and King," who claimed the credit of the invention for his country. In a letter to the editor of *Le Moniteur* of 1812 (No. 150), he calls attention to statements made years before by Fourcroy in his lectures, according to which solutions of gums (Fourcroy considered starch as a kind of gum),⁵ if "oxygenated muriatic gas" (chlorine) was passed through them, became sweet, showing at the same time a very bitter taste. Gassicourt also quotes Parmentier who said in his *Pharmacopoeia*, published about 1800, that twenty years ago he had noticed that starch paste which had stood for some months mixed with a little cream of tartar had become sweet and the sweetness had become more pronounced when acetic acid was substituted for the cream of tartar. Deyeux had repeated the experiment and obtained the same results.

How weak this claim was considered to be, may be surmised from the fact that not a single scientific journal could be found to champion it, and only the editor of *Schweigger's Journal* thought it necessary to rebuke it.⁶ Chauvinism in science had then not yet made its appearance.

THEORY OF REACTION.

The problem involved in the mechanism of the inversion of starch with acids started practically with the first paper published on the subject, the desire to give some adequate explanation of the peculiar reaction being only natural under the circumstances. That the final solution has not yet been found, notwithstanding the century since passed, and the earnest concerted efforts made in this direction, we all know.

In his letter to the *Journal de Physique*⁴ describing the discovery, Nasse writes: "It has not yet been exactly determined whether the sulphuric acid in acting upon the starch is itself decomposed or not,

⁴ *Schweigger's Journal*, 5, 32 (1812).

⁵ Fourcroy, "Elements, etc.," Vol. IV, p. 115. "A kind of dry gum which we shall examine under the name 'fécula amyliacée'." Fécula is derived from faeces-secretion. Chlorophyll was called fécula verte.

⁶ *Schweigger's Journal*, 5, 99 (1812).

⁴ *Journal de Physique*, 74, 196 (1812).

but I have reason to believe that it is, and is reoxidized instantly by the water, as in the case of sulphuric acid acting on metals, for instance iron."

A similar view was expressed by Lampadius,¹ who adds that the process must be carried out with full access of air to facilitate oxidation and that the sulphuric acid used for the conversion must be free of sulphurous acid if good results are to be obtained. This explanation is in purely chemical terms, the reaction being conceived as a series of alternating processes of reduction and oxidation of the sulphuric acid, and with reference to the sugar formed from starch by gluten, Kirchhof says that it is a chemical process purely. Whether attempts were made to prove the formation of sulphurous acid during the reaction is not stated, and from the analogy given above, it would seem that this was not thought to be necessary.

Doebereiner thought to have shown experimentally that access of air was necessary but conceived the process merely as a decomposition of water, and later as an electrochemical reaction.² Some chemists thought it was the heat which effected the transformation, although Vogel, in the paper quoted, had already shown that this is not the case, while others tried to adapt Fourcroy's theories, that the sugar preexists in the starch, and is only released by the sulphuric acid, to which objection was made on the ground that sugar would thus form an insoluble compound, something then entirely unknown. Schrader³ disproved the theory of formation of sulphurous acid by experiment and brings the inversion in parallel with the formation of ether from alcohol. He also thinks that during germination, nature uses the same process when forming sugar. Vogel,⁴ who had worked considerably on the subject, merely contents himself with refuting the theories advanced without propounding a new one. The full difficulty of the problem seemed to have been well appreciated by Brugnatelli,⁵ who calls attention to the peculiarity of the fact that only a minute percentage of acid is required to transform large quantities of starch into sugar, and this is, according to him, the point which yet remains to be explained by scientists.

Of the opinions expressed then and in the few years following regarding the mechanism of the starch inversion it can be seen that only very few tried to bring them in harmony with the observed facts; most of them merely attempted to explain the reaction in the light of preconceived hypotheses, a custom which still survived to some extent. The solution of the problem, at least so far as it admits of solution, and the one which has prevailed thus far, because it conforms to all the observable facts, came only several years later and from a man who by his strict adherence to the principle, that the experiment properly conceived and executed carries with it its own explanation, has directed our knowledge

into new channels. This man was Saussure, the great founder of plant physiology, equally great as chemist, as physicist and as botanist.

Saussure, who was domiciled in Geneva, Switzerland, had already in 1814 published a very important paper "On the Conversion of Starch into Sugar," to which we shall yet have to refer in another connection. The paper which we have to consider here was read before the Royal Society of London, on December 17, 1818, and was printed in its Proceedings and reprinted or abstracted later in many chemical publications. The title is "The Decomposition of Starch by the Action of Air and Water at Atmospheric Temperature."¹ It contains many observations and analytical data, and also the announcement of the discovery of a new sugar from starch (maltose of present day), a discovery which it took fifty years to be verified and fully accepted. This paper also states the theory of hydration² and the words in which this is expressed are so lucid and logical, show such a penetrating insight into the mechanism of the reaction, that they may well be reproduced here for historical reasons, the more so as they apply also to hydration processes other than those of starch. Discussing the results of his experiments, Saussure says:

"In analyzing the sugar formed by the action of sulphuric acid and water on starch I have found that the reaction takes place through absorption (fixation) of the elements of water by the starch. I have arrived at the same explanation or rather at its confirmation by showing that the sugar formed by this process weighs more than the starch used when both are dried at steam heat. This observation might seem opposed to the one which showed that the residue obtained on spontaneous decomposition of starch weighs less than the starch used, but it is perhaps superfluous to observe that the two processes cannot be compared, because in the case of sulphuric acid, sugar is in the last instance the only noticeable product of the reaction, while during the decomposition of starch on the air several products are formed, among which the elements of the (absorbed) water are unequally divided and are partially lost during evaporation."

"By the term 'fixation' of water in the starch to form the sugar I do not mean to convey that this is there in either solid form or in the form of water of crystallization, the way in which they are divided is yet undetermined.

"Such a fixation of water takes place undoubtedly more often than one would think in treating vegetable or animal substances by the ordinary processes of our laboratories. I have found that the new properties which fats acquire when saponified are due principally to the fixation of the elements of water."

We have added little if anything during the one hundred years since this was written to the knowledge

¹ *Bull. de Pharm.*, 4, 551 (1812).

² *Schweigger's Journal*, 4, 306.

³ *Ibid.*, 5, 81.

⁴ *Ann. de Chim. et de Phys.*, 82, 184.

⁵ *Bull. de Pharm.*, 4, 328 (1812).

¹ *Ann. de Chim. et de Phys.*, 2 s., 11, 379 (1819); and other periodicals of same year.

² The term "hydrolysis" was introduced many years later by Armstrong.

of the mechanism of hydrolysis, the catalytic theory propounded later by Berzelius notwithstanding.¹

ANALYSIS OF THE STARCH, NATURE AND ANALYSIS OF THE STARCH SUGARS.

Up to 1811 the following sweet substances had been isolated in fairly pure state: cane sugar, beet sugar, maple sugar, sugar from honey, sugar from grapes, sugar from urine. These were called true sugars because they yielded to vinous (alcoholic) and acetous (acetic acid) fermentation and gave on treatment with strong nitric acid, oxalic acid. The first three were obtained in readily crystallizable form and this served to differentiate them from the other true sugars, which were less sweet and less easy to crystallize. To the latter belonged also the sweet substances obtained by fermentation from starch, and the sugar prepared from different fruits (levulose), the nature of which was entirely unknown, as they had never been separated pure enough.

There were known also in addition: the sweet principle of Scheele (glycerin) and sugar of milk, which were not fermentable and of which the latter, on treatment with nitric acid, yielded mucic acid.

The year 1811 saw the addition of the sugar from starch, in 1812 Vogel inverted milk sugar with acid and in 1818 Saussure isolated a sugar from starch undergoing spontaneous decomposition.

It is well to remember that in those days fermentation and combustion were the only means available to establish quantitative relations in this group of substances, both of which methods we know today to be applicable only with great precautions. This sufficiently indicates the difficulties against which the chemists then working with sugars had to contend, and in the light of our present knowledge of the subject, we are not surprised to see that progress here was only very slow.

Only a few of the papers published on the subject of acid conversion of starch between 1812 and 1820 attempted to bring the sugar thus formed in closer connections with the sugars already known, and still less tried to do this on the strength of analytically obtained data. Quantitative analysis as a guide in chemical experimentation was then only very gradually coming into its own and elementary combustion introduced in 1810² into organic chemistry by Gay-Lussac and Thenard was resorted to only in rare instances.

Starch was one of the small number of organic

¹ The tendency has, of late years, been plainly manifesting itself to make extended use of the theory of Contact Action for the purpose of explaining chemical reactions, the mechanism of which seems to be darker than in others. Under these circumstances it is perhaps a pardonable transgression to point to the fact that in the long drawn-out discussions on this subject it has been shown with sufficient clearness that this theory does not explain anything, and that as a matter of fact it merely introduces another unknown factor into equations sufficiently complicated by themselves. Professor Ostwald's definition of the catalyzer as an "accelerator" of chemical reactions obviously is not intended to, and does not, touch upon the mechanism by which it "accelerates." This theory, like its antipode in mechanics, the Actio in Distans, are purely metaphysical concepts of extremely doubtful value which it has taken long years to eradicate from the domain of experimental science. Their reintroduction seems to serve no useful purpose.

² *Recherche Phys. Chim. Paris*, 2, 291 (1811). The paper was read before the Academy of Science of Paris, Jan., 1810.

substances which the inventors of elementary analysis had subjected to combustion. They found in starch from grain

	Per cent.
C.....	43.58
H.....	6.77
O.....	49.58
Ash.....	0.23

A few years later, Berzelius¹ published his celebrated essays to determine the proportions in which the elements are combined in organic bodies, starch among them. In the precipitate formed by sugar of lead in starch solutions he thought to have found a distinct chemical substance containing:

	Per cent.
Starch.....	72.0
Lead oxide.....	28.0

An analysis of potato starch gave him

	Per cent.
C.....	43.48
H.....	7.06
O.....	49.46

and from these figures he derived the formula for starch, $C_7H_{10}O_6$.

Saussure,² however, in the paper first mentioned had preceded him in the analysis of starch which he undertook to make in the course of his examination of the sugar formed therefrom by sulphuric acid.

Putting aside all theory and with the balance as his foremost criterion, he first prepared pure and dry starch, then submitted it to the action of sulphuric acid, isolated and dried the sugar obtained as near quantitatively as possible and, before anybody else had done so, established the fact that sugar formed weighs more than the starch used, and that the relation between the starch used and the sugar formed was as 100 : 110.14, a relation which, as we know, is only very little from the truth.

Saussure made combustions of carefully prepared starch, starch sugar and grape sugar, with the following results:

	Starch.	Starch sugar.	Grape sugar.
Carbon.....	45.39	37.29	36.71
Hydrogen.....	5.90	6.84	6.78
Oxygen.....	48.31	55.87	56.51
Nitrogen.....	0.40
	100.00	100.00	* 100.00

These figures come, in every case, so close to theory that considering the primitive means with which a combustion had to be made in those days, one cannot but marvel at their accuracy and the infinite skill, patience and care of their author. The sugar, as may be seen, was in the hydrated form.

Saussure also compared the behavior of the two sugars towards chemical reagents and summarizing his results, says: "Starch differs from sugar only by the elements of water, the starch sugar is identical in composition with the sugar from grapes, and chemically, they don't differ at all." The identity of these two sugars was thus established and though in later years questioned by many investigators, it has finally prevailed.

¹ *Ann. de Chim. et de Phys.*, 95, 83 (1815).

² *Bibliothèque Britannique*, 1814, abstr. *Bull. de Pharm.*, 6, 499 (1814).

COST OF STARCH SUGAR.

From the very day its formation was observed, starch sugar was intended as a substitute for cane sugar. The energies of most all the investigators were bent in this direction, and to make the process economical enough, so that commercially the two products would be on as near an equal basis as possible with the balance perhaps in favor of the new sugar.

Lippman states that at the time of the continental blockade, sugar sold on the continent for from 2 to 6 francs per pound, which figure therefore had to be met or bettered by the new competitor and for this reason may be used for comparison.

The most detailed estimate of the cost of production of starch sugar at that time is furnished by Lampadius¹ and is as follows:

	Francs.
Potatoes.....	40.00
To make starch therefrom.....	6.67
24 pounds of sulphuric acid @ 1.50 fr.....	36.00
4 boxes of charcoal.....	11.00
Labor.....	16.00
Use of utensil.....	4.00
	<hr/>
	113.67
Deduct for feed value of remaining mush.....	16.00
	<hr/>
	97.67

He obtained 240 pounds of syrup that cost per pound approximately 0.41 franc (about 8 cents) from which the author figures that the sugar could be sold for 0.67 franc.

The quintal of potatoes (200 pounds) is figured at 4 francs and since Lampadius used 6½ ounces of acid to 4 pounds of starch, the quintal is taken to yield 24 pounds of starch from which 24 pounds of syrup are supposed to be obtained. This was usually of 1.5 sp. gr.

Ittner and Keller,² giving their experience, state that the quintal of potatoes can be had for from 27 to 39 francs, and without any further details figure the (selling?) cost per pound of syrup of 1.5 sp. gr. at 0.75 franc. If so, they must have made a handsome profit because it is reported that they sold their product at 1.60 francs per pound.³

The sugar made from wheat starch should have cost considerably more because the price of this starch, at the time, was 1.60 francs per pound, while that from potatoes sold at 0.60 franc.⁴ In 1837,⁵ solid starch sugar sold in Berlin at \$10.50 per 100 lbs.

In comparing the cost of the two sugars it is necessary to keep in mind that, weight for weight, they differ considerably in sweetness, a fact which was well known at that time. The relation is variously given from 2 : 5 up to 2 : 3 in favor of cane sugar, but Gehlen,⁶ in considering the subject, justly remarks that the respective valuation of the sugars cannot

be based on their sweetness alone, but that their food value likewise is a factor to be considered, in regard to which both sugars are at least equal.

STARCH AND GLUCOSE IN AMERICA.

Starch was made in the American colonies at a comparatively early period of their history. In describing the different processes used to make starch, Fourcroy¹ says: "The Americans prepare from the root of a very astringent plant called 'manioc', a nourishing and very sweet starch which they call cassava."

This probably refers only to the French possessions in the South, though there is very little doubt but that the thrifty and cleanly Puritans of the north prepared from grain their own starch, which had become a household necessity.

In 1802, we find it mentioned, a certain John Biddis, of Pennsylvania, undertook the manufacture of starch from potatoes as a business proposition, which must have been a great success as the industry branched out rapidly. His works were located in Hillsborough County, N.H., and it is stated that the whole of his product was used by cotton goods manufacturers.² In fact up to the introduction of the cornstarch, by Thomas Kingsford in the United States, and James Coleman in England (a patent on this had been granted already in England in 1824 to one, Thomas Wickham), potatoes were the principal source for starch-making in the United States.

The first two decades of the last century saw the United States of North America gradually forging ahead toward their destiny of becoming the leading nation of the world, acquiring, by purchase or war, room for development and freedom of action, yet, as a whole, they had not lost yet their colonial character and colonies, with perhaps the one exception of old Greece, never were the proper ground for advancing science or producing scientists. Yet chemistry was a science which was early cultivated in the United States and found many devotees. Philadelphia was the center and already in the nineties of the 18th century it could boast of a Chemical Society, before whom papers were read regularly. A translation of Lavoisier's work by Kerr was published there in 1799. Silliman in his *American Contributions to Chemistry* omits to mention these facts. In a material way, the formation of sugar from starch was of no importance in America where both cane and maple sugar were to be had in abundance, and this sufficiently explains why this discovery, which at one time focused upon itself the attention and hopes of all continental Europe, passed practically unnoticed in the United States.

The beginning of the industrial exploitation of this invention, *i. e.*, of the industrial manufacture of glucose in the United States, which now and for many years past, is one of the leading industries of the country, surpassing by far all other countries, dates from the year 1831, an account of which is found in Silliman's *Journal of Science*.³ It was a

¹ *Bull. de Pharm.*, loc. cit.

² *Bull. Soc. de'Enc.*, 11, 128, 235 (1812).

³ *Ibid.*, 12, 219 (1813).

⁴ The difference in prices for the finished starch and the starch used for conversion is due to the fact that for the latter purpose the wet material was employed and no profit was allowed in this shape.

⁵ *Journ. f. prakt. Chemie*, 11, 185 (1837).

⁶ *Schweigger's Journal*, 5, 32 (1812).

¹ "Dictionnaire de chimie."

² *Bishop History of American Manufacturers*, 2 (1866).

³ *Journal of Science*, 21, 93, 284 (1832).

partnership enterprise, one, S. Guthrie, furnishing the chemical knowledge and a Captain Potter supplying the engineering skill. Their idea was to make glucose syrup only in backward countries where it could compete in price with other sugars, and, being situated in Sacket Harbor, they tried their scheme there. The plant, as finally used, had a capacity of 30 gallons of sugar syrup of 1.5 sp. gr., or 360 pounds per day. The starch was made from potatoes in a wooden cylindrical tank fitted with a grinding contrivance, producing a wet pulp from which the starch was separated by settling. Glass vessel being out of question on this scale, they at first used lead balloons of 7 to 8 gallons capacity for conversion, but finding them not only inconveniently small but also dangerous inasmuch as the syrup contained too much lead, they constructed a strong wooden tank of 400 gallons capacity, fitted with an air-tight cover and tested to stand a pressure of 10 pounds. A charge consisted of 600 pounds of wet starch—equal to 370 pounds dry—225 gallons of water and 4 pounds of sulphuric acid sufficiently diluted. The charge being made, the aperture of the conversion tank was closed and steam was admitted through a copper pipe connected to a copper boiler of large dimensions in which water was heated to 15 pounds pressure. The conversion took 5 to 6 hours, the pressure in the tank being maintained at 5 pounds.

The converted product was then neutralized with calcium carbonate, filtered, clarified and evaporated to the required consistency.

A bushel of potatoes, weighing approximately 60 pounds, gave 8 pounds of dry starch, from which 5 pints of syrup were obtained or about 7.5 pounds to the bushel.

The editor of the *Journal of Science* remarks in a foot-note that he is using this syrup for himself and family, finds it of fine quality, not as sweet as cane sugar, but less oppressive to the stomach.

The glucose industry of to-day is not a direct continuation of the diminutive beginning described above. For decades succeeding it, no glucose seems to have been made in this country or else only on a scale entirely unnoticeable. The first patent relating to glucose in the United States was taken out in 1864 by F. W. Gossling and then one invention followed another in close succession.

In 1870, the industry makes its first appearance in the Census of Manufactures, but is yet so small that it is counted together with that of beet sugar, two establishments with 116 employees and an output of \$119,720 being counted for both. The industry developed rapidly thereafter, coincident with that of cornstarch, and soon became a dangerous competitor to the cane sugar boilers and refiners, who in 1882 caused a law to be introduced in Congress calling for regulation and special taxation of glucose and corresponding products. This induced the then Commissioner of Internal Revenue, G. R. Raum, to call upon the National Academy of Science for a report on glucose, especially in its effects as a food product, in response to which a commission composed

of five eminent chemists (among whom were Professors Chandler and Remsen) was appointed, who in 1884 submitted their report giving glucose a clean bill of health. At that time 29 factories¹ existed using on an average 1500 bushels of corn per day when working, but work was very irregular and depending upon the price of corn. No less than six liquid and six solid varieties of glucose were then made. To-day the industry of glucose in the United States is leading that of all other countries and controls by its exports the world market. The yearly value of glucose alone is now probably in excess of \$30,000,000 (the census of 1905 gave \$24,566,932 for 9 establishments) and counting corn oil and the various feeds, etc., which to-day approach almost the glucose in importance, and cannot, therefore, consistently be called by-products, the total yearly value of the products of this industry should be very much in excess of the figure given above.

CONCLUSION.

Except for a very cursory description of conditions in the United States, this historical study on starch and glucose is intended to close with the year 1820, as it would be impossible for obvious reasons to pursue the subject in this place right down to our times. As a matter of fact, up to that year all the hydrolytic products of starch, which so far have been positively identified as such, namely, dextrin, glucose and maltose, had already been established though, as stated above, the last one had to be rediscovered twice before it finally found unquestioned acceptance by the chemists.

The 90 years of industrious investigation which have followed have swelled the literature enormously, besides adding by degrees to the knowledge of these substances. A review within the permissible limits of this journal could at best only point to those works which in the history of the products in question were of epoch-making importance, as for instance, the introduction of the polariscope as a help in the investigation, analytically and otherwise, or to the work of Dubrunfaut, O'Sullivan, Fischer and others. This would be doing justice to neither the subject, nor to the great number of men who devoted their life energy to the advancement of our knowledge of these extremely complex and difficultly accessible bodies and whose works can only be fully appreciated when considered in their historical connection.

Within the period specified, the history of glucose, as stated in the preceding chapters, may therefore be regarded as comprising all the more important points. The only addition which perhaps would be required would be the observation that wood, when treated with sulphuric acid in a way similar to starch, is likewise convertible into glucose. This observation is usually attributed to Braconnot,² but Bayrhammer, a Bavarian chemist, is at least entitled to equal credit, since, in a letter to Berzelius,³ dated March, 1819, he had

¹ The Census for 1880 counting, evidently, only establishments working full time quotes 7 factories in operation.

² *Annales de Chim. et de Phys.* (2 s.), **12**, 172.

³ Berzelius, *Jahrbuch der Chemie*, **1**, 107 (1822).

described the same discovery. In the same year, Braconnot extended his experiments to linen rags and found that these too gave glucose under similar treatment.

The fate of glucose commercially was not one of great showing until well within modern times. Already in 1814, Napoleon was compelled to do away with the continental blockade which, though it hurt England much, hurt Europe very much more, and which, moreover, could not be enforced against the gigantic system of smuggling which it had developed. Thus let loose, the flood of colonial products, pent up for years, took its course towards the continent and simply swamped the market. The price of sugar dropped to unprecedented low levels, the more so as the competition of the beet sugar already began to be felt. Starch sugar, the manufacture of which still offered considerable difficulties, could not under the conditions maintain its existence and one factory after another was compelled to close its doors. It is doubtful whether in 1820 there existed a single establishment anywhere preparing sugar from starch for the market. Only after the sugar had created for itself its own sphere of consumption in the fermentative industries (beer, wine, etc.), which came about only very gradually and largely through the instrumentality of Lampadius in Germany, and Dubrunfaut and Payen in France, was the manufacture of glucose on a commercial scale taken up anew. Its development to the gigantic proportions of modern times is recent history.

Even in a scientific way starch sugar seemed to have lost most of its interest, judging from the scarcity of papers published on the subject in the years following its discovery. Only since the entry of Dubrunfaut into the chemical arena, who in 1821 published his first paper on sugars and kept at it for the whole of his busy life, did this interest gradually revive, assuming ever larger proportions, which of course was not without influence on the industrial exploitation of this commodity.

One more point must be gone into here for the sake of completeness, although strictly speaking it goes beyond the period intended to be covered. It relates to the term "glucose" which has been used throughout this sketch synonymously with starch sugar. As a matter of fact, the name glucose was not introduced into the chemical nomenclature before 1838¹ having been proposed by Dumas to designate sweet substances generally, which cannot be obtained in readily crystallizable form in contradistinction to cane or beet sugar. Into the German and apparently also the English literature the designation crept only some years afterwards. That the term has within recent years been restricted to the commercial product exclusively must be assumed as generally known, and is the natural result of the better knowledge which the chemistry of carbohydrates has given us of this substance.

Not much space will be required to trace the development of starch chemistry in directions other

than those of hydrolysis. Particular mention deserves here the method devised by Kirchhof¹ for the purification of starch, for which purpose he advised the use of dilute caustic potash to eliminate the glutinous matter, followed by washing. This is the only other paper the discoverer of glucose published on the subject of starch and starch sugar (the one giving the formation of sugar by germinated barley having already been mentioned above).

Of far greater importance was the observation of the beautiful blue color starch assumes when in contact with iodine, thus giving to the chemist the most sensitive indicator known for either of these two substances. The discovery of iodine in the ashes of seaweed by Courtois took place in 1812, and gave rise to numerous investigations. Incidental to these, Colin and Gaultier de Claubry, of France,² as well as Stromeier,³ of Hungary, observed the reaction, if such it may be called, between starch and iodine, a discovery the nature of which in later years up to the present days has formed a subject of much investigation and controversy, without having been so far satisfactorily solved. The few other papers published dealt more with details and while furnishing material for later investigations were not of sufficient importance to be dwelt on in this place.

WASHINGTON, D. C.

THE DETERMINATION OF ARSENIC IN INSECTICIDES.

By E. B. HOLLAND.⁴

Received Jan. 20, 1911.

During the past three years the writer has given considerable time to the study of arsenical insecticides, with special reference to their manufacture, composition and use, the main object of which was to provide the entomological department of this station with chemicals of known composition, suitable for an extended investigation to determine their effect in practical application under varying climatic and atmospheric conditions.

For more than a decade, the analysis of arsenicals has received marked attention because of the high value of a number of these salts as insecticides. The sale of inferior, adulterated or imitation products lacking in efficiency or causing severe injury to foliage has rendered necessary a certain amount of supervision by the agricultural experiment stations of the country. In several states special laws have been enacted to regulate the sale and to provide for an inspection of such materials. Arsenic as trioxide or pentoxide is the active constituent of these compounds, and various methods of several distinct types and numerous modifications have been proposed for its determination. Some of the methods are applicable to arsenous acid and others to arsenic acid.

METHODS.

As the work planned by the entomological de-

¹ *Schweigger's Journal*, **14**, 385 (1814).

² *Ann. de chim. et de phys. and Journ. de phys.*, **79**, 113 (1814). The paper was read before the Academy in March, 1814.

³ *Schweigger's Journal*, **12**, 349 (1813).

⁴ Assisted by Dr. R. D. MacLaurin, Prof. S. F. Howard, C. D. Kennedy and J. C. Reed.

¹ *C. R.*, **7** (1838).

partment would require many analyses, it was desirable that the methods adopted should be reasonably short and simple, though accuracy would be the controlling factor. The literature on the determination of arsenic was reviewed at some length. The results, while somewhat overwhelming, can be roughly summarized under gravimetric methods, volumetric methods and processes for the elimination of substances liable to effect the determination. A classification of this character is open to criticism but will serve the purpose intended.

The gravimetric methods include the hydrogen sulfide precipitation of arsenous acid¹ weighable as arsenous sulfide after removal of the excess sulfur; the Neher modification² of the Bunsen method,³ precipitating arsenic acid with hydrogen sulfide, weighable as arsenic sulfide; the modified Levöl method, precipitating arsenic acid with "magnesia mixture" weighable as magnesium pyro-arsenate; and the Werther method,⁴ precipitating arsenic acid with uranyl acetate weighable as uranyl pyro-arsenate. The inherent faults of the sulfide methods render them impractical. The modified Levöl method, the most prominent of the gravimetric, is complicated, tedious and tends towards low results. All of these methods are time-consumers and none of them appear to have met with favor, having of late been almost entirely superseded by volumetric.

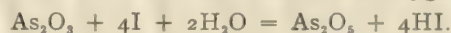
The volumetric methods include that of Kessler,⁵ oxidizing arsenous acid with potassium bichromate and titrating the excess chromic acid with standard ferrous sulfate, using potassium ferricyanide to determine the end-point; the permanganate method, titrating arsenous acid with standard potassium permanganate to a rose color; the Mohr method, titrating arsenous acid with standard iodine in the presence of sodium bicarbonate, using starch paste as indicator; the Bunsen method,⁶ based on the difference in amount of chlorine evolved from hydrochloric acid by a given weight of potassium bichromate in the presence of arsenous acid, the gas being conducted into potassium iodide and the free iodine titrated with standard sodium thiosulfate, using starch paste as indicator; the Krickhaus method,⁷ reducing arsenic acid to arsenous with hydrochloric acid and potassium iodide and titrating the free iodine with standard thiosulfate; the Bennett modification⁸ of the Pierce method,⁹ precipitating arsenic acid with silver nitrate and titrating the silver in the precipitate with potassium sulphocyanate according to Volhard;¹⁰ and the Bödeker method,¹¹ titrating arsenic acid with standard uranyl nitrate using potassium ferrocyanide to determine the end-point. The Kessler and Bödeker methods are objectionable in their re-

quirement of an "outside" indicator. The Bunsen and Bennett methods are lengthy and demand very careful manipulation. The permanganate titration is not as sensitive as the iodine and the Krickhaus method offers no advantages in its application to arsenic acid over a similar reduction and titration with iodine. In other words, the iodine titration method (Mohr) seemed to us rather superior to any other in point of accuracy, manipulation and time, and was adopted for the work in view.

There are a number of processes that are noted more particularly as a means of eliminating impurities likely to effect the arsenic determination, among which may be mentioned the distillation processes of Fischer,¹ Piloty and Stock,² Stead³ and Jannasch and Seidel,⁴ using hydrochloric acid in connection with reducing substances such as ferrous salts, hydrogen sulfide, and potassium bromide and hydrazine hydrochloride. The above list of methods is far from complete but attention has been called to practically every type applicable to commercial products.

IODINE METHOD (MOHR).

As previously stated, the iodine method appeared to offer the greatest advantages and was selected. A clear understanding of the character and limitations of the reaction underlying the method is necessary at the outset. Iodine is an indirect oxidizer, acting on the elements of water with the formation of hydriodic acid and the liberation of oxygen.



The oxidation cannot be conducted in an acid or neutral solution because of the reversible action of the hydriodic acid. If the latter is neutralized with sodium bicarbonate as rapidly as produced, the reaction will proceed to completion. Caustic alkali or carbonate cannot be employed as they absorb iodine, the former being especially active. The reaction between starch and iodine in the presence of hydriodic acid or soluble iodide is one of the most sensitive in analytical chemistry, forming the characteristic blue iodide starch. A more delicate indicator could not be desired. Since the method was first applied to the analysis of arsenicals numerous modifications have been devised to insure complete solution of the arsenic, to prevent oxidation, to eliminate or render innocuous substances that might effect the titration, and to enlarge its field of application so as to readily include the arsenates. The Association of Official Agricultural Chemists began work on insecticides in 1899 and has rendered valuable service.

NEW PROCESSES.

The introduction of the Thorn Smith process⁵ marked a turning point in the analysis of arsenicals. It was intended particularly for Paris green and is the official method for that substance. Solution of the arsenic is effected by boiling the sample with a slight excess of sodium hydroxid which readily unites with

¹ Fresenius, "Quan. Chem. Anal."

² *Ztschr. anal. Chem.*, **32**, 45 (1893).

³ *Ann. Chem. Pharm.*, **192**, 305.

⁴ *J. prakt. Chem.*, **43**, 346 (1848).

⁵ *Pogg. Ann.*, **118**, [4] 17 (1863).

⁶ *Ann. Chem. Pharm.*, **86**, 290.

⁷ *Eng. Min. Jour.*, **90**, 357. See Sutton for earlier references.

⁸ *J. Am. Chem. Soc.*, **21**, 431 (1899).

⁹ *Proc. Coll. Sci. Soc.*, Vol. I.

¹⁰ *Liebig's Ann.*, **190**, 1 (1878).

¹¹ *Ann. Chem. Pharm.*, **117**, 195.

¹ *Ztschr. anal. Chem.*, **21**, 266 (1882).

² *Ber. deut. chem. Gesell.*, **30**, 1649 (1897).

³ Sutton, "Vol. Anal.," Ed. **9**, 159 (1904).

⁴ *Ber. deut. chem. Gesell.*, **43**, 1218 (1910).

⁵ *J. Am. Chem. Soc.*, **21**, 769 (1899).

the free arsenous acid and also with the combined, after displacing the copper. In presence of a reducing substance like sodium arsenite, the copper is precipitated as cuprous oxide and a portion of the arsenous acid oxidized to arsenic. This oxidation necessitates a subsequent reduction of the filtrate with hydrochloric acid and potassium iodide (hydriodic acid) and the removal of the excess iodine with thiosulfate. The solution is neutralized with dry sodium carbonate, an excess of sodium bicarbonate added, and titrated with iodine. The process is accurate, though the double titration is objectionable.

Avery and Beans devised a very ingenious process¹ noted for its simplicity. The Paris green is pulverized, solution effected with concentrated hydrochloric acid in the cold, neutralized with sodium carbonate, the precipitated copper redissolved with sodium potassium tartrate and titrated as usual. The copper held by the alkaline tartrate colors the solution but does not effect the titration. Hydrochloric acid, however, is a poor solvent for free arsenic and unreliable, which constitutes a very serious objection to the process. Avery noted this error and advised² that samples showing a tendency to separate white arsenic should be treated with $N/2$ hydrochloric acid, 5-10 cc. for each 0.1 gram, and boiled gently. In case arsenic remains undissolved, a cold saturated solution of sodium acetate, 3 grams salt for each 0.1 gram of substance, is added and boiling continued until solution is effected. By another modification³ suggested by Avery and reported by Thatcher,⁴ 1 gram sample is boiled 5 minutes with 25 cc. of sodium acetate solution (1-2), dissolving the free arsenic which is removed by filtration. The residue is dissolved in dilute hydrochloric acid and both solutions titrated.

Haywood attempted, in several ways,⁵ to modify the original Avery-Beans process so as to insure solution of the free arsenic. After treating the sample with a slight excess of hydrochloric acid at laboratory temperature, sodium carbonate was added and the solution boiled. In another case sodium bicarbonate was employed but the results were unsatisfactory in both substances, due to more or less reduction of copper and accompanying oxidation of arsenous acid. Accurate results were secured, however, by filtering off the hydrochloric acid solution and boiling the residue with 5 grams of sodium bicarbonate, titrating both solutions.

Haywood proposed still another modification⁶ which might be considered a simplified Avery-Thatcher process,⁷ 0.4 gram sample is boiled 10 minutes with 25 cc. sodium acetate solution (1-2) to dissolve free arsenic and concentrated hydrochloric acid carefully added until solution is effected. After neutralizing with a solution of sodium carbonate, avoiding an

excess, alkaline tartrate and sodium bicarbonate are added and titrated as usual.

The Avery, Avery-Thatcher and Avery-Haywood processes employ the same reagents, differing only in their application. The coöperative investigation⁸ of the association in 1904 showed that the three above modifications, together with the Haywood, gave closely agreeing results with little if any advantage in the two-solution processes over the one. In 1905 the results⁹ with the Avery-Thatcher and Avery-Haywood modifications were not as satisfactory though the average difference was not excessive.

On comparing the merits of the Thorn-Smith process and various modifications of the Avery-Beans with apparently little choice as to accuracy, the Avery or Avery-Haywood process, with one titration of a single solution, certainly appeals to chemists in "control" work from the standpoint of manipulation, possible mechanical losses and time. This does not warrant any less care in conducting the analysis but if anything demands greater attention. The essential features of the Avery-Haywood process have been employed at the Massachusetts station for the work on arsenites, though considerably modified as to detail.

PRACTICE AT MASSACHUSETTS STATION.

Having adopted Thatcher's suggestions³ as to ratio of sample to acetate solution, 1-25, and finding 25 cc. rather inadequate for proper boiling and agitation, double quantity of each is taken. To prevent slight loss of sample in transferring to flask, due to both adhesion and dusting, boats of folded filter paper are employed and found very serviceable, particularly for Paris green and arsenic for standard solution. After boiling the solution 5 minutes with acetate, the directions call for the careful addition of concentrated hydrochloric acid until solution is effected. Such a procedure in our hands gave extremely variable results and generally a low test for arsenic. This error necessitated several weeks of experimenting and was found to be due to the addition of *concentrated* acid, dilute acid (1-3) giving uniform results in practically every instance and a higher test. Probably this has been one of the sources of trouble with the chemists reporting on association samples by the above process in past years. Neutralizing with sodium carbonate, in dry form or concentrated solution, will introduce an error if added in excess. The use of sodium bicarbonate is preferable for the purpose as the latter salt does not absorb iodine and eliminates an unnecessary reagent. As concentration has a certain influence on titration, it is advisable to maintain approximately the same volume in every case. The tendency of some solutions to become muddy on titration can often be relieved by additional bicarbonate, though the conditions involved seem to have no appreciable influence on the results. The quality of all reagents employed in the determination should be proved by blank tests which

¹ *J. Am. Chem. Soc.*, **23**, 485 (1901).

² *Ibid.*, **25**, 1096 (1903).

³ Optional official method, Assoc. Off. Agr. Chem.

⁴ *Proc. Assoc. Off. Agr. Chem.*, **20**, 196 (1903).

⁵ *J. Am. Chem. Soc.*, **25**, 963 (1903).

⁶ *Proc. Assoc. Off. Agr. Chem.*, **20**, 197 (1903). Optional official method of the Association.

⁷ *Loc. cit.*

⁸ *Proc. Assoc. Off. Agr. Chem.*, **21**, 98 (1904).

⁹ *Ibid.*, **22**, 27 (1905).

¹⁰ *Ibid.*, **21**, 99 (1904).

should not exceed 0.10 cc. iodine solution for the amounts employed. Some lots of bicarbonate have been found unfit for such work. Due recognition should be given the blank in calculating results.

Considerable trouble is often experienced in determining insoluble matter with hydrochloric acid due to the splitting off of white arsenic, especially with Paris green. To offset the difficulty it was found advisable to combine the determination with that of preparing the arsenic solution by simply filtering off the residue. The points noted above may be briefly summarized:

Transfer 2 grams of finely pulverized sample together with 50 cc. of sodium acetate (1-2) to a 500 cc. graduated flask and boil 5 minutes. Cool under tap, add about 60 cc. of hydrochloric acid (1-3) and shake until solution is effected. Make to volume and filter. Pipette 25 or 50 cc. into an Erlenmeyer flask, neutralize with dry sodium bicarbonate, add 25 cc. of sodium potassium tartrate¹ (1-10) to redissolve precipitated copper, approximately 3 grams of sodium bicarbonate, water sufficient to make a volume of 100 cc., 2 cc. starch paste (1-200) and titrate with *N*/20 iodine to a permanent blue color. Toward the end of the reaction cork the flask and shake vigorously to insure proper end-point. Calculate results as arsenous oxide. The residue in the graduated flask is brought onto the filter, well washed, calcined in a porcelain crucible and weighed as insoluble matter.

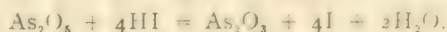
The above process has given excellent results with copper aceto-arsenite, copper arsenite and calcium arsenite. Sodium acetate does not prevent hydrolysis of copper and calcium arsenites as in the case of Paris green, but serves to take up free arsenic. The presence of such impurities as cuprous and ferrous compounds, sulfurous and nitrous acids or other oxidizable substances is a source of error by the iodine titration method.

IODINE METHOD FOR ARSENATES.

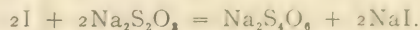
The increasing use of lead arsenate as an insecticide resulted in a demand for a rapid volumetric method for the determination of the arsenic acid. The Gooch and Browning process,² as modified by Haywood,³ serves to readily reduce arsenic acid to arsenous in which form the iodine titration method is applicable. The process, in our hands, did not at first prove satisfactory but eventually yielded concordant results after minor changes. As the differences are largely a matter of detail not involving principle, only the modified process will be given.

Transfer 2 grams of finely ground sample together with 60 cc. of nitric acid (1-3) to a 500 cc. graduated flask, bring to boil, cool, make to volume and filter. Pipette 50 or 100 cc. into a 150 cc. Jena Griffin beaker, add 10 cc. of sulfuric acid (2-1), evaporate, heat in an air bath at 150-200° C. to expel last traces of moisture, and then on asbestos board to the appearance of dense white fumes to insure complete removal of nitric acid. Add a small quantity of

water and when cold, filter through a sugar tube under suction into a 300 cc. Erlenmeyer flask and wash to about 100 cc. Add 10 cc. of potassium iodide (165-1000) and boil until free iodine is expelled—solution practically colorless—with the reduction of arsenic to arsenous acid.



Dilute, cool immediately, neutralize with sodium hydroxid and render slightly acid with sulfuric acid. Add starch paste and if any free iodine remains, add dilute (*N*/50) thiosulfate carefully with vigorous shaking to the absence of blue color.



Add excess of sodium bicarbonate and titrate as usual with *N*/20 iodine, reporting as arsenic oxide. The residue in the graduated flask is brought onto the filter, washed, calcined and weighed as insoluble matter.

Care should be taken to add sufficient sulfuric acid to cover the bottom of the beaker when heated on asbestos. A decided excess of acid is also necessary when boiling with potassium iodide to insure vigorous action and rapid volatilization of iodine. Neutralization with caustic soda is permissible under the conditions described. The hydroxid is a much more convenient and rapid agent than the carbonate. Practically no difference was noted in the titration when the lead sulfate was allowed to remain, but the data at hand does not cover a sufficient number of samples to warrant a statement that this will always hold true.

The iodine method, as modified for arsenites and arsenates, has been given a careful study and proved repeatedly in the work at the Massachusetts station to yield excellent results in the analysis of the insecticides mentioned, if reasonable attention is paid in following the details. While no radical changes in the method have been recommended, this article is offered in hopes that some of the points noted may prove of assistance to other analysts working along similar lines.

DEPARTMENT OF PLANT AND ANIMAL CHEMISTRY,
MASSACHUSETTS AGRICULTURAL EXPERIMENT STATION.

PURIFICATION OF INSOLUBLE FATTY ACIDS.

By E. B. HOLLAND.

Workers in oils and fats experience the same difficulty in obtaining chemically pure products as investigators in other lines of organic chemistry. The best insoluble fatty acids on the market—judging from our experience—are unsatisfactory in both physical characteristics and neutralization number. In general appearance the acids that are offered resemble granulated curd, though varying in color from white to yellow, and contain considerable dust and dirt. The molecular weight, as measured by titration, in an alcoholic solution, may deviate from the theoretical by 10-15 points. These statements apply to chemicals marked "C. P." and bearing the name of a reputable manufacturer or dealer.

The writer required stearic, palmitic, myristic,

¹ Used only with the copper arsenites.

² *Am. J. Sci.*, 40, 66 (1890).

³ *Proc. Assoc. Off. Agr. Chem.*, 23, 165 (1906). Provisional method of the Association.

lauric, and oleic acids for certain tests and finding it impossible to purchase them of the desired quality was forced to undertake a study of various methods for their purification. As the character of the unsaturated acids is so unlike that of the saturated, only treatment of the latter will be considered at this time. The methods that seemed the best adapted for the purpose were (a) distillation of the fatty acids *in vacuo*, (b) crystallization from alcohol and (c) distillation of the ethyl esters *in vacuo* and all were given extended trial.

(a) DISTILLATION OF THE FATTY ACIDS IN VACUO.

Direct distillation under reduced pressure was successfully employed a few years ago by Partheil and Ferie¹ starting with Kahlbaum's best acids. Upon careful test the writer found that the method possessed certain objectionable features which render it rather impracticable for ordinary use. If it was merely a question of distillation of the acids, the process would be less difficult but for fractionation, using a Bruehl or similar type apparatus, it proved almost impossible, in case of the higher acids, to prevent solidification in the side neck (outflow tube). The danger arising from a plugged apparatus at the high temperature involved has also to be taken into account. An attempt was made to heat the tube and keep the acids liquid by means of a hot water jacket, also by an electrically heated asbestos covering but neither process fully met the requirements of the case. The slow distribution of heat *in vacuo* is, of course, one of the obstacles in the way. For the distillation of solids of high melting point Bredt and A. van der Maaren-Jansen² devised an elaborate piece of apparatus having a flask and receiver of special construction and an overflow tube heated by electricity but it is hardly suited for a general laboratory or for handling any considerable quantity of material.

There are two other conditions necessary for a successful distillation of fatty acids, namely, absence of moisture and a current of hydrogen or carbon dioxide to prevent bumping and to lessen decomposition. Overlapping of the acids in different fractions can not be obviated entirely and if an unsaturated acid was present in the original, it will probably appear in nearly every fraction.

Students under the direction of Professor Burrows, of the University of Vermont, have applied this process for a partial separation of the insoluble acids of several oils with a fair measure of success. With all due allowance for the possibilities of the method in the production of pure saturated fatty acids, the inherent difficulties render it inadvisable in most instances.

(b) CRYSTALLIZATION FROM ALCOHOL.

Crystallization in this connection is practically limited in its application to the removal of a small amount of impurities, especially unsaturated acids. It can hardly be considered other than a supplementary treatment, though excellent for that purpose, to follow either of the distillation methods. Dry neutral alcohol suitable for such work can be

prepared by distillation after treatment with caustic lime. In dissolving the acids care should be taken to avoid heating to a higher temperature than is required for solution or to prolong the heating unduly as it will cause the formation of esters. Several minutes' boiling of the different fatty acids in alcohol caused the following loss in neutralization number.

Stearic acid.....	1.70
Palmitic acid.....	0.56
Myristic acid.....	2.24
Lauric acid.....	0.89
Oleic acid.....	0.28

Esterification undoubtedly causes a serious error by this process of purification. Under more careful treatment the change is not as rapid as shown above but is evidently cumulative and may even exceed the figures given. Further study may warrant the substitution of a more stable solvent such as acetone. For the filtration a water- or ice-jacketed funnel is almost necessary particularly for the acids of low melting point and suction is a time-saver. Repeated crystallization is needed to bring out the true crystalline structure and silvery luster of the leaflet. Vacuum drying at a low temperature is one of the most efficient means for removing adhering alcohol and traces of moisture without injuring the structure. Crystallization as a whole is wasteful of acids and solvent unless both are recovered, but is essential for the production of a superior product.

(c) DISTILLATION OF THE ETHYL ESTERS IN VACUO.

As ethyl esters distil freely *in vacuo*, the process admits of a more ready application and to products of a greater range of purity than does a distillation of the acids. After considerable experimenting it was found that the esters are easily prepared by heating in an open flask equal parts (100 grams) of fatty acids and alcohol together with a small quantity (10 cc.) of concentrated hydrochloric acid, using capillary tubes to prevent bumping. The reaction requires about 30 minutes, after which the excess of hydrochloric acid can be removed with a separatory funnel. The distillation is conducted in a 500 cc. "low" side neck flask with a small (8 inch) Liebig condenser and a large size Bruehl fractionation apparatus. Heat is furnished by means of a linseed oil bath and suction by a pump of any type using a mercury manometer to prove constancy of vacuum. The neck of the flask from the shoulder to an inch or more above the side tube should be wound with asbestos paper to prevent cracking, due to sudden changes of temperature. The condenser should be kept full of water without circulation to serve as a hot water jacket. The vacuum should be as high as the flask will safely withstand but above all uniform, otherwise the fractions are of questionable value. The temperature range of an ester also varies with the distance between surface of liquid and side tube. At least one redistillation of like fractions is necessary.

As the esters are very stable, more difficulty was experienced in finding some means for their quantitative decomposition than in any other portion of the work. Heating with mineral acids hydrolyzes

¹ Arch. Pharm., 241, 545 (1903).

² Liebig's Ann. Chem., 367, 354 (1909).

the fatty acids very slowly even under pressure. If, however, the esters are first saponified¹ by heating over a naked flame with twice their volume of glycerol and an excess of caustic potash until all the alcohol is expelled, and then the resulting soap dissolved in water and heated on a water bath with a slight excess of sulfuric acid, the separation is readily accomplished. This plan was suggested by the Leffmann-Beam saponification for volatile acids and after extended trial proved the most thorough and rapid means for decomposing the esters. The resulting acid should be washed in a separatory funnel with boiling water until clear and the cake allowed to drain. As previously stated, several crystallizations are necessary if a crystalline product of satisfactory melting point and neutralization number is to be secured. When crude acids are employed it is also advisable to crystallize at the outset to exclude a major part of the unsaturated acids which otherwise would prove troublesome.

To summarize: saturated fatty acids may be purified by distillation of the acids or their ethyl esters. The latter method is less hazardous and easier to manipulate although more steps are required. Crystallization is a finishing rather than an initial process of purification.

DEPARTMENT OF PLANT AND ANIMAL CHEMISTRY,
MASSACHUSETTS AGRICULTURAL EXPERIMENT STATION.

DEPRESSION OF THE FREEZING POINT BY VINEGARS AS A CHECK ON THEIR COMPOSITION.

By ALEXANDER SILVERMAN.

A number of years ago the writer, while visiting some agricultural laboratories in New York State, was informed that "Depression of Freezing Point" determinations were made daily on samples of milk collected from various points in the district and that if the depression lay within certain limits (total variation about 0.08° C.) the analysis was dispensed with as it had invariably been found that a milk coming within this limit was of the composition required by the state.

This simple check on composition led to determinations of the depression of the freezing point by four standard vinegars, samples of which were very kindly furnished by the most reliable manufacturers of this country.

In each case a complete analysis was made as outlined in succeeding tables and by methods that follow. Then a specific gravity determination and then the depression test.

METHODS OF ANALYSIS.

Acidity.—5 cc. of vinegar were diluted to 50 cc. with distilled water in a 125 cc. Erlenmeyer flask, 3 drops of a 1 per cent. alcoholic solution of phenolphthalein added, and then $N/10$ NaOH solution from a burette until appearance of the pink color. If an excess of NaOH had been added back-titration with $N/10$ HCl was resorted to with subsequent addition of $N/10$ NaOH to the pink end-point.

The $N/10$ HCl solution was prepared by diluting

75 cc. of the concentrated chemically pure acid with an equal volume of distilled water, weighing 36 grams and diluting to one liter. The strength was determined by precipitation of silver chloride, as directed in the "Official and Provisional Methods of Analysis of the Association of Official Agricultural Chemists" published by the United States Department of Agriculture (Bulletin 107, Bureau of Chemistry). The acid was then diluted to exactly $N/10$ and again checked.

The $N/10$ NaOH solution was prepared by dissolving 50 grams NaOH in water, diluting to 1 liter and checking again the $N/10$ HCl, using 3 drops of 1 per cent. phenolphthalein as an indicator. After comparison the NaOH was diluted to exactly $N/10$ and again checked by the $N/10$ HCl.

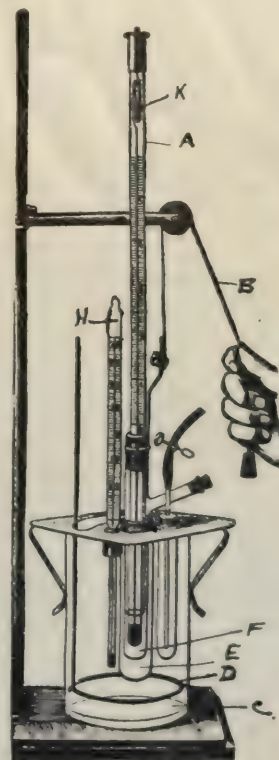
Solids.—Ten cc. of vinegar were placed in a small tared platinum dish, evaporated for two hours on a water bath and dried five hours in a steam oven.

Ash.—Ten cc. of vinegar were placed in a platinum crucible, evaporated to sirupy consistency and carefully incinerated below dull red heat.

Moisture.—This was determined by difference after deducting acidity and solids.

Specific Gravity.—This was determined in a 25 cc. tared specific gravity bottle filled first with pure distilled water and weighed and then with the vinegar to be tested. The weight of the latter divided by that of the water gave the specific gravity.

Depression of Freezing Point.—This was effected in the apparatus here illustrated when A is a Beckman thermometer usually covering a range of 5 or 6° C. and reading to 1/100° C. The glass jar C was filled with a mixture of 10 parts of cracked ice, 1 part of salt and 1 part of water which mixture gave a temperature of about -10° C. recorded on thermometer H. The mixture was stirred from time to time by stirrer D. The space between tubes E and F was filled with ethyl alcohol which gave better results than when tube E contained air. Twenty-five cc. of distilled water were placed in tube F and the mercury in bulb K adjusted, by slightly jarring the thermometer, until the freezing point of water was recorded somewhere between 5° and 6° mark. The freezing point was recorded and the water was replaced by 25 cc. of vinegar which was next cooled to freezing and the temperature recorded. The difference indicated the depression of the freezing point. While the water and vinegar were being frozen the



¹ Observing the usual precautions given for the determination of insoluble fatty acids. *Mass. Agr. Expt. Sta. Rpt.*, 21, 130 (1909).

stirrer B was constantly raised and lowered through the solution. The freezing point was indicated by a sudden rise in the mercury when the substance solidified, owing to heat liberated when the substance was converted from the liquid to the solid state. The entire determination required an average of twenty minutes.

For analyses the vinegar was measured rather than weighed so as to avoid the loss usually incurred by evaporation when weighing liquids. The volume in cubic centimeters was then multiplied by the specific gravity to obtain the weight in grams.

Following are the tables which show the data obtained:

PREPARED MALT VINEGAR.

Number of sample.	Depression of freezing point.	Acidity. $\text{HC}_2\text{H}_3\text{O}_2$. Per cent.	Solids. Per cent.	Ash. Per cent.	Moisture. Per cent.	Specific gravity.
19	1.13° C.	5.0	1.6	0.2	93.4	1.13
20	1.13° C.	5.0	1.6	0.2	93.4	1.13
21	1.13° C.	5.0	1.6	0.2	93.4	1.13
22	1.13° C.	5.1	1.6	0.2	93.3	1.13
23	1.14° C.	5.1	1.8	0.2	93.1	1.14
24	1.14° C.	5.1	1.8	0.2	93.1	1.14
25	1.14° C.	5.1	1.8	0.2	93.1	1.14
26	1.14° C.	5.1	1.8	0.2	93.1	1.14
27	1.14° C.	5.1	1.7	0.2	93.2	1.13
28	1.14° C.	5.1	1.7	0.2	93.2	1.13
29	1.13° C.	5.0	1.7	0.2	93.3	1.13
30	1.13° C.	5.0	1.7	0.2	93.3	1.13
Average,	1.135° C.	5.06	1.7	0.2	93.24	1.133

DISTILLED VINEGAR.

Number of sample.	Depression of freezing point.	Acidity. $\text{HC}_2\text{H}_3\text{O}_2$. Per cent.	Solids. Per cent.	Ash. Per cent.	Moisture. Per cent.	Specific gravity.
31	2.14° C.	5.3	0.2	0.02	94.5	1.006
32	2.14° C.	5.3	0.2	0.02	94.5	1.006
33	2.14° C.	5.3	0.2	0.02	94.5	1.006
34	2.14° C.	5.3	0.2	0.03	94.5	1.006
35	2.10° C.	5.2	0.2	0.02	94.6	1.006
36	2.10° C.	5.2	0.2	0.02	94.6	1.006
37	2.10° C.	5.2	0.1	0.02	94.7	1.006
38	2.16° C.	5.3	0.1	0.02	94.6	1.006
39	2.20° C.	5.5	0.2	0.02	94.3	1.007
40	2.20° C.	5.5	0.2	0.02	94.3	1.007
41	2.20° C.	5.5	0.2	0.02	94.3	1.007
42	2.20° C.	5.5	0.2	0.02	94.3	1.007
Average,	2.15° C.	5.35	0.18	0.02	94.48	1.0063

CIDER VINEGAR.

Number of sample.	Depression of freezing point.	Acidity. $\text{HC}_2\text{H}_3\text{O}_2$. Per cent.	Solids. Per cent.	Ash. Per cent.	Moisture. Per cent.	Specific gravity.
1	2.65° C.	5.8	2.6	0.3	91.6	1.15
2	2.65° C.	5.8	2.7	0.3	91.5	1.15
3	2.65° C.	5.8	2.6	0.3	91.6	1.15
4	2.65° C.	5.8	2.6	0.3	91.6	1.15
5	2.70° C.	5.8	2.9	0.3	91.3	1.16
6	2.70° C.	5.8	2.9	0.3	91.3	1.16
7	2.67° C.	5.8	2.8	0.3	91.2	1.16
8	2.68° C.	5.8	2.8	0.3	91.2	1.16
Average,	2.67° C.	5.8	2.73	0.3	91.41	1.155

MALT VINEGAR.

Number of sample.	Depression of freezing point.	Acidity. $\text{HC}_2\text{H}_3\text{O}_2$. Per cent.	Solids. Per cent.	Ash. Per cent.	Moisture. Per cent.	Specific gravity.
9	3.35° C.	6.1	1.9	0.2	92.0	1.20
10	3.35° C.	6.1	1.9	0.2	92.0	1.20
11	3.35° C.	6.1	1.9	0.2	92.0	1.20
12	3.35° C.	6.1	1.9	0.2	92.0	1.20
13	3.30° C.	6.0	1.9	0.2	92.1	1.18
14	3.30° C.	6.0	1.9	0.2	92.1	1.18
15	3.30° C.	6.0	1.9	0.2	92.1	1.19
16	3.30° C.	6.0	1.9	0.2	92.1	1.19
17	3.37° C.	6.1	1.9	0.2	92.0	1.20
18	3.37° C.	6.1	1.9	0.2	92.0	1.20
Average,	3.33° C.	6.06	1.9	0.2	92.04	1.194

In every case where the depression of the freezing point remained within the limits cited in the tables, the vinegar was found to analyze up to the required standard.

As the result of these experiments the writer recommends that chemists associated with vinegar or pickling and preserving factories establish a depression of the freezing-point range for each vinegar manufactured or used by them.

One inducement for giving the method a trial is that it requires but twenty minutes for each determination. Every vinegar chemist knows that a complete analysis requires a much greater period of time.

UNIVERSITY OF PITTSBURGH,
DEPARTMENT OF CHEMISTRY.

A BACTERIOLOGICAL METHOD FOR DETERMINING AVAILABLE ORGANIC NITROGEN.

By J. M. McCANDLESS AND F. C. ATKINSON.

This laboratory was called upon last summer to report upon the availability of the ammonia in two samples of material which we will call "Nitrolene and Ammolene;" the nitrogen in these materials was derived exclusively from leather, but they had been treated by a special process for rendering the leather soluble and available.

We analyzed the two materials by the Pepsin-acid method and by the Neutral and Alkaline Permanganate methods. The results were flattering to the materials and on the whole quite satisfactory; but we desired to obtain for our clients evidence more in the nature of a crop or pot test: there was, however, no time to make such tests, therefore, we decided to make a soil extract, and digest our materials in this solution for the limited period of time at our disposal.

At that time we had no knowledge of the fact that Dr. Lipman, of New Jersey, had published a paper on "Bacteriological Methods for Determining the Available Nitrogen in Fertilizers."¹ If we had, we should probably have followed the method outlined by him, but we used the following method: Total nitrogen was determined in samples of cottonseed meal, nitrolene and ammolene with the following results:

Cottonseed-meal.	Nitrolene.	Ammolene.
Per cent.	Per cent.	Per cent.

Total nitrogen as ammonia.....	8.20	9.40	3.42
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One-gram portions of each were weighed, treated on filters with boiling water, and the filtrate made up to 500 cc.; aliquot portions were taken and the total nitrogen in the aqueous solution determined; the nitrogen existing as free and saline ammonia was also estimated in separate portions by distillation with magnesia; the following results were obtained:

Cottonseed-meal.	Nitrolene.	Ammolene.
Per cent.	Per cent.	Per cent.

Nitrogen (in terms of NH_3), in the aqueous solution.....	1.01	5.79	2.49
Percentage of total nitrogen in the materials, soluble in water.....	12.3	61.94	72.8
Free and saline ammonia in the aqueous solution.....	0.28	0.45	0.88
Water-soluble organic nitrogen (in terms of ammonia).....	0.73	5.34	1.61

¹ THIS JOURNAL, 2, 146.

A sample of soil was procured, and a definite quantity shaken up with some of each of the aqueous solutions and filtered; definite portions of the filtrate were then incubated for a period of 210 hours at 38–40° C. One series of flasks was incubated under aerobic conditions loosely stopped with cotton wool; another series under anaerobic conditions in flasks with the surface of the liquid protected by oil. In all these latter flasks the tests for nitrates and nitrites were practically *NIL*.

In the aerobic flasks the ammonia produced by the action of the soil bacteria, from the water-soluble organic nitrogen was:

	Cottonseed-meal. Per cent.	Nitrolene. Per cent.	Ammolene. Per cent.
After lapse of 40 hours.....	0.00	1.12	1.10
After lapse of 88 hours.....	0.00	1.56	0.42
After lapse of 160 hours.....	0.02	0.37	0.08
After lapse of 210 hours.....	0.20	0.30	0.00
	0.22	3.35	1.60

The experiment was stopped at this point by exhaustion of the flasks prepared. As will be seen, the action on the cottonseed-meal solution was slow as compared with the others. In the case of the ammolene, practically all of the water-soluble organic nitrogen had been converted into ammonia after 88 hours. In the case of the nitrolene, which was much richer in organic nitrogen, about 63 per cent. of the soluble organic nitrogen had been converted into ammonia in 210 hours, but the action then became very slow, presumably due to the toxic action of an excess of ammonia on the organisms producing it.

A solution was now prepared containing in 1 liter, potassium phosphate 1 gram, sodium chloride 2 grams, magnesium sulphate 0.5 gram, and calcium chloride 0.050 gram; this solution was shaken up with a definite quantity of the soil and filtered, 50 cc. of the filtrate was placed in small flasks along with the filter papers containing the residues from the treatment of one gram of each material with hot water. After incubating these residues for 26 days there remained in the

	Cottonseed-meal. Per cent.	Nitrolene. Per cent.	Ammolene. Per cent.
Insoluble ammonia.....	2.09	2.74	0.60
Ammonia rendered soluble by incubation	5.10	0.87	0.33
Total solubility in terms of ammonia....	6.11	6.66	2.82
Percentage of solubility on total nitrogen in materials.....	74.5	70.9	82.5

An interesting observation was made in connection with the incubation of the insoluble residues of the nitrolene and cottonseed-meal. After 5 days' incubation, the contents of a set of these flasks were filtered, and in the filtrates we found:

	Cottonseed-meal. Per cent.	Nitrolene. Per cent.
Free ammonia.....	1.25	0.13
Also, organic nitrogen rendered soluble (in terms of ammonia).....	Lost	0.13
After 8 days, similar analyses showed free ammonia	1.00	0.20
Also, organic nitrogen rendered soluble (in terms of ammonia).....	0.40	0.25

In other words, the bacteria had produced from the insoluble proteid matter of the cottonseed-meal, 2.25 per cent. of ammonia, and had rendered 0.4

per cent. + per cent. in the lost determination of the insoluble organic nitrogen soluble; in the case of the nitrolene, in 8 days they had produced in like manner from the insoluble proteid matter 0.33 per cent. of ammonia, and had converted 0.38 per cent. of the insoluble organic nitrogen into a soluble form.

Evidently there are two distinct processes, first, the bacteria convert the insoluble proteids into a soluble form, and it must be in this soluble form before they can decompose it into ammonia. It would doubtless be a matter of interest to the professional bacteriologist to ascertain whether the ammonifying organisms also possess the power of rendering proteid matter soluble, or whether this function is performed by some other organism.

The method seems worthy of further application as a test of the availability of doubtful nitrogenous materials, as the conditions are completely under the control of the operator, and in this respect, and in the shortness of the time required, have a great advantage over crop, or pot tests, while the results are equally as convincing, since there is little or no doubt that the ammonification of organic nitrogenous substances by the intervention of the soil bacteria precedes their nitrification and absorption as plant food.

INFLUENCE OF VARIATION IN SPECIFIC HEAT OF WATER ON CALORIMETRY OF FUELS.

By LEO LOEB.

Along with the values of the heats of combustion of the various substances used in calorimeter standardization which accompany samples of cane sugar sent out by the Bureau of Standards is a short account of the experiments of Fischer and Wrede.¹ Mention is made of the fact that their values are given in terms of electro-mechanical units, since the specific heat of water was not determined more closely than one part in two thousand. Yet as early as 1902, W. E. Barnes published in the *Physical Review*, 15, 71, the results of his experiments at McGill University on the specific heat of water.

An electrical method devised by Professor Callendar and Dr. Barnes was employed to get the data from which the values were computed. The heat unit used was the amount of heat required to raise the temperature of 1 kg. of water from 15–16° C. Other values have been determined by Dieterici² but his method does not appear to have the certainty of Barnes; nor are his results as consistent. In general Dieterici's results are higher than those of Barnes, but this is in part due to the fact that his heat unit was the Bunsen Calorie.

Indeed, the failure to agree on a universal heat unit is the cause of frequent inconsistencies in calorimetry. At least three standards are recognized:

1. The Calorie as defined above.
2. The B. t. u.: the amount of heat required to raise

¹ *Sitzungsberichte der Preussischen Akademie der Wissenschaften, Berlin*, 5, 129 (1908).

² *Annalen der Physik*, (4) 16, 573 (1905).

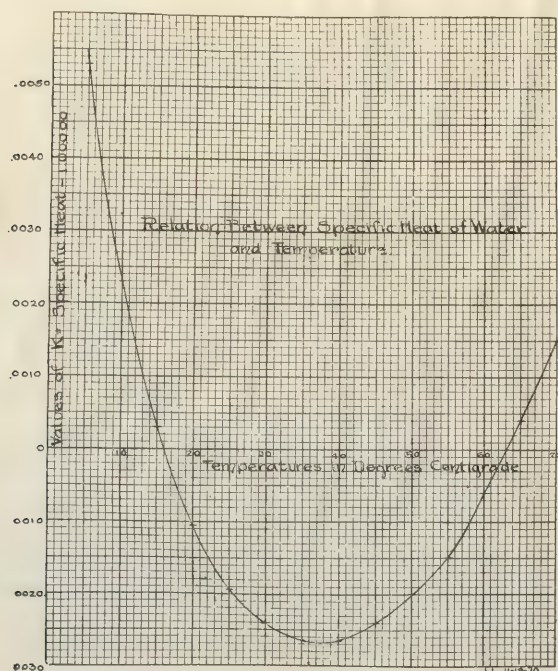
the temperature of one pound of water from 62–63° F.

3. The Bunsen or mean Calorie: one one-hundredth part of the heat to raise the temperature of a kilogram of water from freezing to boiling point.

The first two differ by about 0.035 of 1 per cent., whereas the variation between the third and either of the other two is as great as 0.2 of 1 per cent.

On account of these differences the results which follow must be considered tentative, subject to a final agreement upon the definition of a heat unit. The writer accepted the values of Barnes, because they were generally considered the better, even by those who were inclined to give some weight to the work of other experimenters. Under the circumstances it was only logical to accept the heat unit that this experimenter had used.

To determine the probable effect of the variation on calorimeter work, these values (having a probable precision of one part in fifty thousand) have been plotted in the accompanying diagram over the range



required. The data is taken from Peabody's "Thermodynamics of the Steam Engine," p. 79. The exaggerated scale is obtained by plotting values of $k = \text{specific heat} - 1.00000$; that is, the true axis of ordinates must be assumed to be 10,000 small divisions below the arbitrary one. Then the amount of heat which is required to raise 1 kilogram of water from T_1 to T_2 is $\int_{T_1}^{T_2} c \, dt$. If T_1 be taken as 0° C., we have the value which in thermodynamics is denoted by the letter q , the heat of the liquid above 0° C. It can best be determined graphically as the area under the specific heat curve between 0° and the temperature considered.

The method of procedure in this determination was to read from the curve the values of the specific heat

at every degree and to consider the area between any two adjacent degrees and the axis as a trapezoid.

The resulting values of q are given in the accompanying table:

Temp. in ° C.	Specific heat.	q above 0° C.	Temp.	Specific heat.	q .
0	1.00940	0.00000	26	0.99795	26.04932
1	1.00855	1.00898	27	0.99784	27.04720
2	1.00770	2.01710	28	0.99774	28.04499
3	1.00690	3.02440	29	0.99766	29.04269
4	1.00610	4.03090	30	0.99759	30.04031
5	1.00530	5.03660	31	0.99752	31.03786
6	1.00450	6.04150	32	0.99747	32.03536
7	1.00390	7.04570	33	0.99742	33.03280
8	1.00330	8.04930	34	0.99738	34.03020
9	1.00276	9.05233	35	0.99735	35.02757
10	1.00230	10.05486	36	0.99733	36.02491
11	1.00185	11.05694	37	0.99732	37.02224
12	1.00143	12.05858	38	0.99732	38.01956
13	1.00100	13.05980	39	0.99733	39.01689
14	1.00064	14.06062	40	0.99735	40.01422
15	1.00030	15.06109	41	0.99738	41.01159
16	1.00000	16.06124	42	0.99743	42.00899
17	0.99970	17.06109	43	0.99748	43.00644
18	0.99941	18.06064	44	0.99753	44.00395
19	0.99918	19.05994	45	0.99760	45.00152
20	0.99895	20.05900	46	0.99767	46.00016
21	0.99872	21.05783	47	0.99774	47.00086
22	0.99853	22.05645	48	0.99781	48.00152
23	0.99836	23.05490	49	0.99790	49.00250
24	0.99820	24.05318	50	0.99800	50.00405
25	0.99806	25.05131			

The most precise way of determining the heat of combustion is to multiply the weight of water by the difference of " q " for the maximum and minimum temperatures plus the rise of temperature times the water equivalent, but since the rise of temperature in a bomb calorimeter seldom exceeds 3° C., the result will be

$$(T_2 - T_1)(W \times c + E),$$

where

$T_2 - T_1$ is the corrected rise of temperature,

W is the weight of water used in the bomb,

c is the specific heat corresponding to the mean temperature observed.

E is the water equivalent of the bomb.

The net effect of the correction is to make all calorimeter determinations too small between mean temperatures of 13° C. and 16° C. by an amount of 15 B. t. u. per pound of coal at 13°, and all determinations too great where the mean exceeds 16°, if this factor be neglected. The excess will be as much as 22 B. t. u. per pound at 22°. At the latter point it involves practically the same correction as that due to the change in density of water. Between 15° and 18° the effect is practically negligible.

The most marked difference is that in the case of its application to such instruments as the Junker's calorimeter for heat of combustion of gas and oil. There the temperature rise is generally 15–18° above the temperature of the inlet water.

During the combustion of 7 liters of illuminating gas, 1863 grams of water were heated from an inlet temperature of 20.32–39.57° C. at the outlet. The upper heating value of this gas is $\frac{1863 \times (39.57 - 20.32)}{7} = 5123$ small Calories per liter, when the calculation is made in the usual way.

Making use of the table given:

q at 39.57° is 59.585 by interpolation between 39 40
 q at 20.82° is 20.379

19.206

Then the correct upper heating value is

$$\frac{1863 \times 19.206}{7} = 5112 \text{ small calories per liter.}$$

The possible variations are from 0.13–0.25 per cent. This means that in the report on an oil having 18,000 B. t. u. per pound, the heating value would be from 23–45 B. t. u. too high.

To summarize: The correction above considered when applied to work on bomb calorimeters is one-half that due to change in density of water, and equals in magnitude any one of the other corrections: fuse wire, titration and sulphur.

TROY, N. Y.,
 Nov. 22, 1910.

ADDRESSES.

ON CERTAIN PROBLEMS CONNECTED WITH THE PRESENT-DAY RELATION BETWEEN CHEMISTRY AND MANUFACTURE IN AMERICA.

By ROBERT KENNEDY DUNCAN.

In presenting some reflections on the present-day relation between chemistry and manufacture in America, it is necessary, both because of the large scope of the subject and because the quotation of individual instances would be offensive, to proceed in a spirit of broad generalization; the validity of these generalizations will depend on the reasonableness of their context. Furthermore, it should carefully be prevised that there is no attempt to take a dogmatic, *ipse dixit* attitude, and, related to most of the statements that will be made, there should be carefully understood the words *exceptis exceptendis*.

The problems to be discussed are in large measure the result of a lack of mutuality between the factory organizations on the one hand and the universities and technical institutions on the other. This lack of mutuality depends primarily upon a lack of understanding on the part of factory organizations of the advantages that are to be derived from the employment of sensible chemical research, and of a corresponding lack of understanding on the part of institutions of learning of the proper training and type of men that are requisite for the successful practice of chemical industrial research in these factories. A mutual understanding, in America at least, might speedily lead to coöperation, and coöperation to a sensibly functioning coördination. The American factories, taking them by and large, and making such distinguished exceptions as could be numbered on the fingers of both hands, certainly do not have coördinating relations with the universities, such, for example, as we find developed in Germany. Furthermore, in so far as industrial research is concerned, they do not have coördinating relations with one another. There exists no common consciousness among the corporation officials of this country of the proper methods of conducting factory research. In

order to show how true this is, permit me to place before you the results of a preliminary inquiry which was initiated last spring as to the conduct of factory bureaus of research:

First, the entirely significant fact should be stated that at that time there existed no available list of the research bureaus of this country connected with factory organizations. After writing unavailingly to various reasonable sources, such as the *Journal of Industrial and Engineering Chemistry*, the *Bureau of Commerce and Labor*, the *Census Department*, etc., it became necessary to inquire here and there everywhere among industrial colleagues for individual and incidental information. Owing to their kindly coöperation, there was eventually provided a list of some seventy-five corporations possessing either bureaus of research or individual research chemists. From these corporations there were received some forty-five frank replies, given on the understanding that each reply was to be confidential and was to be used only in a summation of results. The results of this preliminary inquiry are illuminating of the chaotic conditions that pervade factory research.

It may be interesting to know that in very few instances are contracts made with chemists. In general the chemist is "hired" by the week or by the month. There are a few, a very few, instances of contracts of one or two years duration, and one instance of three years. Of security of tenure, there is virtually none, except in the rare instances of contract. With reference to the question of security of tenure, one meets constantly such statements as "Yes; if ability and energy are shown;" "Yes; if he makes good, otherwise not;" "A man's record and value are his only security;" "As long as work is satisfactory;" etc., statements which seem reasonable until one considers, as will be seen below, the lamentable conditions under which, too often, these men work.

Next, as to the salaries, or, as a term which is more fitting on the whole, "wages."

In most instances wages are paid by the week: translated into terms of monthly payment, the young graduate receives sums ranging from \$45–100. This latter statement exemplifies the extraordinary diversity of conduct and the chaotic conditions that everywhere prevail in factory research. So far as one may strike an average among such qualitatively different factors, \$60 would perhaps be representative. The question, "Does the initial salary vary with the degree possessed?" elicited the surprising information that in a large number of cases the corporation cares very little, or not at all, what degree the man may have; as one official said, "We call them all doctors, anyhow." What is important to the corporation—vice-president—general manager or what not, is his individual impression of the man and of the likelihood of his "making good." Of course, here, as elsewhere, there is the widest diversity of practice: in one bureau of research, "the degree of B.S. corresponds with \$50–75, while the Ph.D. as nearly as can be stated varies from \$100–200;" or, again, "Yes; a man with a higher degree than B.S. starts with greater salary, though it depends on his other qualifications."

In industrial practice, the particular degree possessed is of much less value than young men understand.

In practically no instance is there any mechanism of promotion.

Related to salaries, and as a natural sequence, there are the hours of labor: and typical of the diversity of practice and the lack of any common agreement as to what is fitting, I append here a fraction of the list of answers: 8-12, 1-5.15; 7½ hours per day; 9 hours; 8-12 M., 1.15-5.15; 9-4.30; 9 hours; 8 hours; 8-5; 8-5; 7.30-5; 9-12, 1-5; about 8 hours daily; 7.30-11.30, 12.30-5.30; 7.30-11.30, 12.30-4.30; 8.45-5.30; up to 24; 8 hours daily; 8½ hours daily (etc., etc.).

Is the research man on the same basis as factory employees in being held rigidly to these hours? There are as many *Yeses* as *Nos*. Relative to hours of labor, and because often enough the young graduate has to choose between an industrial and an academic career, there is the question of vacations. The answers run along as follows:

Two weeks; ten days; two weeks to month; two weeks; seven weeks; generally get what they demand; two weeks for men who have been with us 6 mos.; two weeks; one month; two weeks; ten days if we can spare him; two weeks; two weeks; two to three weeks; ten days (etc., etc., etc.).

The question: "Do researchers take a half-holiday on Saturday?" is answered mostly in the affirmative, though there are some negatives and answers such as follows:

"Yes, during June, July and August."

"During summer months the research men take a half-holiday on alternate Saturdays," etc.

You will probably be surprised to know that there is practically no mechanism of promotion for chemists such as often obtains in factories for officials. One corporation does state that "each man is considered every six months, and if previous work warrants the action, he is recommended to the manager for a raise of salary." Another corporation "is governed only by results;" still another says that "promotion is entirely for merit; seniority counts for little with us." One corporation adds one dollar per week every six months up to a maximum of \$40 per week.

An interesting result of this inquiry appears in the reply to the question: "Do the members of the bureau sign a contract resigning all rights to any discoveries made while in your employ?" The prevailing answer is "Yes." It is a matter of surprise that contracts embodying resignation to rights of discovery were so prevalent. In reply to the question as to whether any additional remuneration was granted to successful researchers, the prevailing answer was "no," with an occasional "increased pay." Two corporations speak of "opportunity to acquire stock" or "a cash present," but there is no instance of royalties or a share in the profits.

The responsibility of the Director of Research to a corporation is generally responsibility to one official therein; but it may be to the president, the vice-president, the superintendent, the consulting engineer or the manager of the works; in certain cases his re-

sponsibility is apparently quite indefinite. The directive power of the director is curious in its indefinite character; often it is not directive at all.

The short time afforded for this address might be wholly taken up through a consideration of the interesting answers offered to many questions.

The inquiry, however, was for personal purposes, was wholly unauthorized and preliminary in character. Reference is made to it here merely to an extent sufficient to justify a statement which will be made later on. The results obtained, while sufficiently demonstrative of uninformed and indeed chaotic conditions, are only inferentially demonstrative of inefficiency in contemporary factory research.

Personal observation, however, for several years leads me to state that presumably 95 per cent. of so-called factory research is worse than loss, *worse than loss* because the failure of the individual instance places a *finale* on the possibility of that particular factory to understand the advantage of applied science. The normal failure that attends factory research is due to ignorance of the canons of judgment in choosing chemists, inexperience in dealing with them, and a generous lack of knowledge of the facilities with which it is necessary to furnish them—laboratory, library, and living facilities. I have met tragical instances of chemists possessed of high training, creative power, and practical character, working under the most shameful conditions, burdened with routine drudgery, subjected to the interference, and orders even, of factory foremen, and what is even worse, working under an entire misapprehension and ignorance on the part of the officials of the company, as to their possibilities and value. I have seen them working under every circumstance of discouragement, inadequate facilities and bad treatment.

On the other hand, I have met equally tragical instances of good corporations employing chemists, or "chemists," who were unfitted or unqualified for the work they had to do—"fakirs" masquerading as chemists, chemists of the "Brahmin" type—analytical chemists trying to do synthetic work and *vice versa*—chemists with scholarship but no creative power and chemists with creative power but no scholarship—chemists with both scholarship and creative power but lacking in the personal or masculine qualities necessary to govern workmen, manage foremen, or to commend themselves to the company's officials.

On the basis of the inquiry which I made, a fraction of which is inserted above, and on the basis of a fairly extended personal observation, I urge upon this society the advisability of establishing an authorized comprehensive investigation into the present conditions that obtain in industrial chemical work, as these conditions refer both to routine and to research work.

I suggest that a commission formed for such a purpose should investigate not only elementary matters, such as salaries, contracts, hours of labor, vacations, laboratory space and equipment, library facilities, relations of chemists to workmen, foremen

and officials, etc., etc., etc., but that it should proceed to investigate the living conditions of factory chemists, *i. e.*, their homes; their social status in the factory family; the degree to which they are permitted to give publicity to their researches; the extent to which they are encouraged to attend the meetings of the learned societies; the time they are given for reading contemporary discovery; the extent to which routine men are attempting research and the amount of routine work required of real researchers; the extent to which corporation chemists are admitted to the results of their researches, etc., etc.

The results of an accredited commission on such a subject could hardly fail to be illuminating and important to the 5000 members that constitute this society. If, further, this commission, on the basis of the best practice discovered, were to build out of this investigation a carefully formulated statement of recommendation, it would be welcomed by chemists and corporations alike. The fact is that at this time many corporations are deeply puzzled as to what to do with their chemists—how to fit them into the discipline of the organization without injuring their spontaneity.

An inquiry recently instituted among the universities enables me to state that the young men pursuing the study of chemical engineering are few in number when compared with those in mining, electrical, civil and even sanitary engineering. The reason for this lies in large measure at the door of the manufacturer, for as stated above he does not understand the conditions he must meet to insure the chemist he employs successful and happy functioning. In some measure, too, it may lie at the door of the university, for it sometimes happens that the director of the courses in chemical engineering is an engineer, not a chemist, and in cases where its responsibility is under the chemical department the director is generally "academic" in quality; in either instance the course may lack the training and inspiration necessary to send good men into industrial chemistry.

This is unfortunate at this time, for in the coming business contraction which informed opinion leads us to expect, while constructional work will diminish with a consequent lessened demand for engineers, industrial research will flourish. It is in hard times that a wise corporation spends money for the elimination of waste and for progressive factory practice.

Let us now consider briefly the extent to which this wide-spread inefficiency in industrial research is due to the university. The present-day vice-president, or general manager of a corporation, however astute he may be, and in fact practically always is, is extraordinarily ingenuous when it comes to "hiring" a chemist. Not infrequently he will write for one to the university which, let us say, his son attends. I do not speak disparagingly, nor with the least hint of disrespect, of my university colleagues, when I say that the importance of the matter and mere candor impel me to state that it is at this point that his troubles begin. His application to the university is handed to the professor of chemistry. Speaking in

generalities, and speaking most decidedly *exceptis exceptiendis*, the professor of chemistry, no matter how distinguished he may be, is not infrequently a gentleman interested and concerned wholly with pure science. He has sometimes, either consciously or unconsciously, the attitude that the utilization of science to human needs is more or less degrading to science itself. In addition, he is a man who vibrates between his home and his laboratory and generally has but little, if any, real knowledge as to the requisites for an industrial chemist. He is, often enough, fundamentally, both through temperament and education, incapable of making a wise choice for the manufacturer concerned, and he may proceed to nominate for the position in question some man for whom he has the least use. He does not understand that success in genuine industrial research presupposes all the qualities which are applicable to success in pure science, and, in addition, other qualities more or less unessential in the university laboratory. Perhaps I may be permitted to suggest that the difference between industrial chemistry and pure chemistry may be compared to the difference between poetry and prose, in the sense that in order to write good poetry it is essential to possess all the qualities of the prose writer, together with others superimposed upon them. The canons of judgment in the choice of an industrial chemist appear to be:

(1) Training (Scholarship).

(2) Creative Power.

(3) Masculine Qualities, which enable the chemist in the factory to deal with workmen and govern foremen.

(4) Personal Qualities, as they affect his relations with colleagues and officials.

(5) Personal Integrity.

(6) Practicality.

(7) Health.

In proceeding to nominate a candidate for an industrial position, it has too often been obvious to me that the professor of chemistry has nominated his man on the basis of scholarship alone.

I venture to suggest that a committee authorized to investigate the conditions that obtain in present-day industrial chemistry could not do better than to include in its investigation the relations that the universities have to industry—or the lack of these relations. There are many and puzzling important problems in this connection. As stated above, there are the canons of judgment which a university should exercise in nominating men for industrial positions. Then there is the question as to how much a university should regard its own selfish interests in refraining from nominating men who are actually or potentially on its instructional staff. Still again, there is the question of "release;" *i. e.*, the conditions on which a university may legitimately be expected to release a member of its staff to accept a more advantageous offer. There is certainly no consensus of opinion on this subject, for where the head of one chemical department may regard it as an exasperating compliment, another is likely to consider it an outrage.

Personally I believe, *pace* the Carnegie Foundation, that a university, outside of its business offices, is not a business organization and that the question of release should be looked at from the standpoint of the best interests of the man concerned, with, of course, an eye to a more or less suitable substitute.

A problem of extreme importance, and one to which I have never seen attention drawn, is the extent to which outside industrial or commercial work is permissible to the instructor in the chemical department of a university. Most professors or assistant professors of chemistry have from time to time offers of routine or research problems, generally attended with the offer of a microscopic remuneration, for industrialists are prone to believe that professors "love" to do such things. Now, we all know that the more the professor becomes involved in money-making outside the less value he is to his students; we know, too, that unless he is engaged in research of some kind, whether "pure" or "applied," he is possibly of still less value to his students, and, finally, we know that his university salary, whatever it may be, is inadequate to his needs. An extrinsic, but important consideration is the fact that carrying on outside work at the expense of the university plant and at a low remuneration, because of his salary, he is taking the bread out of the mouths of his professional brethren, who have to pay for *their* laboratories, apparatus, reagents, and books. I ask again, to what extent may the professional chemist do commercial work and what should be the scale of his remuneration?

Closely allied with this problem is another that lies within the university itself. I refer to the differences existing in the university between instructors having vocational opportunities outside and those that have not. There seems to be a tendency on the part of universities, in order to obtain first-class men, particularly in engineering, physics and chemistry, to pay higher salaries to men having vocational opportunities and at the same time to permit them to exercise their vocation. This, not unnaturally, the professor of Latin or philosophy resents. It would be interesting to see the whole matter threshed out.

Another matter of serious moment, particularly as it refers to commercial routine laboratories, has to do with academic instruction in chemical analysis. I may say advisedly, on the basis of numerous communications, that there is considerable dissatisfaction over the type of instruction that in many instances is offered young men who after graduation enter commercial laboratories in positional capacities—dissatisfaction with antiquated and cumbersome methods that are taught and with the neglect of the time element in making analyses—dissatisfaction, too, over the tardiness with which university laboratories adopt new valid methods and apparatus, and over their neglect to teach their students some sense of proportion in distinguishing between accuracy and *practical* accuracy. Now, it is within the knowledge of us all that young men can never become chemists until they are first trained and disciplined into the exercise of the last fraction of accuracy that is in

them. On the other hand, the university can no longer consider itself as apart from life, or as other than, in part, an institution for fitting young men with opportunities for life. It would seem that it is the duty of a university to fit men for positions as practical analysts as well as to fit them for practical engineering. To what extent should the schools conform in their methods of teaching analysis to practical considerations? This is a problem.

Finally, in this connection, and as a matter of personal opinion, it seems regrettable that chemical instruction should be so largely analytic in character; I mean by this that there seems to be not so much a disproportionate amount of chemical analysis taught in the academic courses, though certainly there is a great deal of it, but that the other courses partake to such an extent of the analytic character in their methods. One wanders through course after course—not formally analytical—courses such as metallurgy, advanced inorganic chemistry and physical chemistry and physiological chemistry, only to find that they are taught analytically by analytic-minded men.

It is for this reason that I attach so much importance to the discipline and methods of organic chemistry, for organic chemistry is almost the sole subject in the chemical curriculum in which a student gains educational training in synthetic working and synthetic thinking. Now, in industrial chemistry the fields that most need research, and that in consequence offer the best opportunities, are in large measure organic—tanning, starch, glue, soap, essential oils, petroleum, and so on almost indefinitely. Furthermore, both in the organic and inorganic fields of industrial chemistry, and outside of the routine testing-laboratories, the problems that are perhaps most important to industrialists are *synthetic* problems. This is naturally the case, for the art of manufacture is fundamentally "making things." Yet the men whom the schools furnish to solve these problems are for the most part men so drilled in analytic habits of thought and work that they cannot naturally and efficiently act or think synthetically. Glass men want new glasses, the metallurgical people new alloys, the enamel workers new enamels, and so on; and yet too often the men appointed to the task are beaten before they begin by their very habits of thought. I do not wish to attach too comprehensive a validity to this remark, but I believe that there is "a soul of truth" contained in it. Presumably, the ideal industrial chemist would be a synthetic man, carefully grounded in analytic work.

At the conclusion of these remarks on the relation of chemistry to industry in America, some reference ought perhaps to be made to the progress and development of the scheme of industrial fellowships which I initiated at the University of Kansas. The essentials of this scheme were published first in the *North American Review*, for May, 1907, and its subsequent progress was indicated in the *Journal of the Society of Chemical Industry*, 28, No. 13, and in *THIS JOURNAL*, 1, No. 8, as well as in *Science*, 29, No. 749.

These publications appeared in the summer of 1909, since which time I have made no report. Owing to the fact that the period of publication has in no instance yet arrived, I may refer to the progress of these researches only in the briefest possible terms:

Fellowship No. 1. On the Chemistry of Laundering.—Mr. F. W. Faragher's fellowship was extended for six months beyond its termination, at double the value, at the end of which time he entered the factories of his donating corporation, where he is doing capable work. On the basis of a part of his researches, the University of Kansas conferred upon him the degree of Ph.D.

No. 2. On the Study of Diastase.—Mr. R. C. Shuey had his fellowship extended by the donating corporation for one year beyond its termination. At the end of this time he had perfected a method for drying alfalfa, in such a way as to conserve its diastatic content, as well as its taste, odor, color, etc. If he succeeds in proving the practicability of his process from the standpoint of cost, his work will amply satisfy his donors.

No. 3. On the Chemistry of Bread.—The donors of Mr. H. A. Kohman's fellowship, the National Association of Master Bakers, in recognition of the value of his other work in behalf of the association, at the termination of his fellowship conferred upon him all proprietary rights in his process of standardizing the large-scale manufacture of salt-rising bread. Mr. Kohman discovered the efficient bacillus for its manufacture, isolated it, grew it in large quantities, and through its use has been able to turn out salt-rising bread, of beautifully uniform quality, at the rate of a thousand loaves a day for over a week. He has been offered large considerations for the rights of this process, and on the basis of his general work and at the request of a certain corporation, he has been offered a new fellowship, yielding \$2500 a year, to continue his researches. His original fellowship was \$500 a year.

No. 4. On the Utilization of the Constituents of Butter-milk.—Mr. E. L. Tague, on the termination of his fellowship, has succeeded in extracting from butter-milk veritable casein. This casein, in quantities of over a hundred pounds at a time, was forwarded to the paper-makers for actual commercial practice. Their reports afforded a complete vindication of his methods.

No. 5. On the Extraction of the Utilizable Constituents from Crude Petroleum.—Dr. F. W. Bushong, through two years' labor upon petroleum, has placed the matter of this fellowship upon such a footing that I have recently been offered a multiple fellowship, providing for the employment of at least six men, to take full advantage of his work. This fellowship I shall accept so soon as rooms are provided for his efficient working.

No. 6. On Enamel-lined Steel Tanks.—On the basis of the work accomplished by Mr. A. J. Weith and Mr. P. Brock, the donors of this fellowship insisted upon taking them over into the corporation six months before its expiration. They have succeeded in con-

structing an enamel which lies beautifully on steel, which is of extraordinary resistivity and which affords good promise of being adapted to large-scale application. In addition, they have developed a substance which is not glass or enamel at all and which also lies beautifully on steel and seems remarkably well adapted in its resistivity, etc., for use as a coating for steel tanks.

This completes the list of Fellowships which have expired.

Of the Fellowships which are now in operation:

No. 7. On the Relation between the Physical Properties of Glass and its Chemical Constituents.—Dr. E. Ward Tillotson is making splendid progress in this fellowship, both from the standpoint of practical results and, as well, along lines of great academic interest. He has won the full regard and confidence of his donors and it is expected that it will soon be possible to publish some of his more important results that do not have a direct practical application.

No. 8. On the Chemistry of Cement and Lime.—Dr. J. F. Mackey is carrying out through this research a comprehensive investigation into a certain phase of cement manufacture after a fashion such as has never before been attempted, and, in addition, seems well on the way to the solution of the large-scale manufacture of slaked lime—a problem which has been of serious annoyance to lime manufacturers.

No. 9. On the Extractive Principles from the Ductless Glands of Whales.—Mr. E. R. Weidlein was sent up to Newfoundland and Labrador early in June, for the purpose of collecting material. He returned in September, completely successful in his quest. He brought back with him over a hundred pounds of suprarenal glands, over a hundred pounds of thyroids, some thymus glands and a large quantity of other very interesting material. He has already discovered that the extractive principles from the suprarenal glands of whales differ in an interesting fashion from the extractive principles obtained from land animals.

No. 10. On the Chemical Treatment of Wood.—This fellowship began considerably less than a year ago, but Dr. L. V. Redman has already succeeded in devising and developing a remarkable and promising process for the improvement of the finish on wood. The finish he obtains, while brilliant and entirely resistive to all ordinary chemical reagents, is forty-three times harder than varnish. He already has patents pending.

No. 11. On Utilities for Borax.—This fellowship, unlike the others, was but of one year's duration. On the basis, however, of what Mr. B. C. Frichot has accomplished, I am just in receipt of a letter from his donors, expressing their cordial appreciation and eagerly requesting a continuance of the fellowship.

No. 12. On the Chemistry of Vegetable Ivory.—Mr. J. P. Trickey is taking full advantage of the opportunities for investigation which lie in this subject and, on the basis of results already achieved, has won from his donors their entire confidence and appreciation.

In recognition of the progress and demonstrated value of this work as a whole, the University of Kansas

this spring constituted it a department by itself. The university has built almost a dozen laboratory rooms for the accommodation of the fellows and, in recognition of the value of their instructional services, has, through action by the board of regents, determined that every fellow shall in his instructional work receive the titular distinction which his fellowship stipend warrants.

In the University of Pittsburgh, in which this work is to be carried on as well, I have already received several important fellowships:

No. 1. *On the Chemistry of Baking*, yielding \$750 a year for two years, with an additional cash bonus of \$2000.

Nos. 2, 3 and 4. *On the Abatement of the Smoke Nuisance*, yielding \$2000, \$1500 and \$750 for three men per year respectively, for 2 years, with an additional consideration of not more than 10 per cent. of the net profits.

These fellowships have been established, but not yet assigned.

Additional fellowships have been signed by donors and are now in the hands of the board of trustees for acceptance. It gives me great pleasure to announce them here for the first time:

No. 5. *On the Relation of the Pots to the Glassmaking and the Elimination of "Streak,"* yielding \$1500 a year for 2 years, with an additional cash bonus of \$2000.

Nos. 6, 7 and 8. *On the Chemistry of Baking*, wholly independent of, but with the acquiescence of, No. 1—for three men, yielding respectively \$2500, \$1500 and \$750 a year for two years, together with an additional consideration of not more than \$10,000 cash.

In addition to these fellowships, I have pending, as stated above, one providing for 6 men, in petroleum research and another multiple fellowship of \$10,000 a year for 2 years, for 3 men, yielding \$5000, \$3000 and \$2000 per year respectively, together with a large additional consideration.

It is apparent, on the basis of the work already initiated at Pittsburgh, that the building, when obtained and completed, will not be large enough to accommodate the demands that will be made upon it. It ought to be said, however, that this building is not yet provided.

From a consideration of the results obtained in the University of Kansas, it seems entirely warrantable to say that the scheme has been so far demonstratively successful in its working, and on the further consideration of the readiness with which industrialists enter into these arrangements, as evidenced both in the University of Kansas and in the University of Pittsburgh, it seems equally obvious that the scheme itself meets with the approbation of the shrewd and capable men who are at the head of these industries.

The scheme itself, as expressed in the agreement between the various corporations and the universities concerned, has undergone a remarkable development. These fellowships, beginning with \$500 a year, have gone progressively up through \$650, \$750, \$1000, \$1500, \$2000, \$2500, and now I am threatened with

fellowships yielding \$5000 a year and \$3000 a year to the fellow appointed.

One remarkable phase of its development lies in the creation of multiple fellowships, designed for the intensive work of several men upon one problem.

Perhaps the most important change which I have made in later agreements relates to the time of publication. This will be seen in the following agreement for a multiple fellowship, which I announce for the first time and which is now typical of the arrangements it seems to me fair and reasonable to make from the standpoint of an advantageous mutuality:

MULTIPLE FELLOWSHIP AGREEMENT NOS. —

For the purpose of promoting the increase of useful knowledge, the University of Pittsburgh accepts from the A. B. C. COMPANY,¹ having head offices at Pittsburgh, Pennsylvania, the foundation of a Multiple Industrial Fellowship, to be known as the A. B. C. FELLOWSHIPS.

It is mutually understood and agreed that the conditions governing this Multiple Fellowship shall be as follows:

To this Fellowship three Fellows shall be appointed.

The exclusive purpose* of this Fellowship is an investigation with a view to improvements in the process and products of baking, to the furtherance of which the holders thereof shall give their whole time and attention, with the exception of three hours a week which each shall give to instructional work in the University.

The Fellows shall work under the advice and direction of the Director of Industrial Research, and they shall forward periodically, through the Director of Industrial Research, reports of the progress of their work to the A. B. C. COMPANY.

For the support of this Fellowship, which shall extend through a period of two years, A. B. C. COMPANY agrees to pay Four Thousand Seven Hundred and Fifty Dollars (\$4,750) per year, payable to the University annually in advance on the date of appointment of the first Fellow. This sum shall be paid by the University in monthly installments to the three holders of the Fellowship, and in the following proportions: to one \$2,500, to another \$1,500, and to the third \$750, per year respectively.

Any and all discoveries made by these Fellows during the tenure of this Fellowship shall become the Property of the A. B. C. COMPANY, subject, however, to the payment by it to them of an additional consideration. This additional consideration to the Fellows, considered as a unit, shall depend upon the value of the services rendered and shall not exceed the sum of Ten Thousand Dollars (\$10,000). The character of this additional consideration (whether royalties, gross amount, or what not), its amount, the time or times of its payment, and the proportions in which it shall be distributed to the three Fellows concerned, shall be determined by the Board of Arbitration provided for herein. At any time during the tenure of this Fellowship, any holder may, at the option of the donor, take out patents at the expense of the donor, on condition that at the time of making application therefor he assigned all his rights to the donor under the conditions of this Agreement.

At or before the expiration of the Fellowship, the business services of any or all of these Fellows may be secured by the donor, for a period of three years, on condition that the terms of such services are satisfactory to the parties at interest.

The University extends towards the A. B. C. COMPANY the privilege of establishing a new Fellowship on the expiration of this.

In the event of any disagreement between the donor and

¹ Name of Company concealed.

the holders of this Fellowship, it is understood and agreed that such disagreement shall be settled, in so far as the dispute relates to matters of fact, by a Board of Arbitration, consisting of a Representative of the University, a Representative of the donor, and a Third Person whom these two shall select, that the decisions of this Board shall be binding upon the parties at issue and that they shall obtain such decision before having recourse to the Courts.

It is also understood and agreed that during the tenure of this Fellowship, the holders may publish such results of their investigations as do not, in the opinion of the donor, injure his interests, and that, on the expiration of the Fellowship, the holders thereof shall have completed a comprehensive monograph on the subject of their research, containing both what they and others have been able to discover. A copy of this monograph shall be forwarded to the A. B. C. COMPANY and a copy shall be signed and placed in the archives of the University until the expiration of three years from that date, when the University shall be at liberty to publish it for the use and benefit of the public. In the event that, in the opinion of the donor, publication three years after the termination of this Fellowship would unduly injure his interests, he is at liberty to appeal for an extension of time to the Board of Arbitration provided for herein which, after consideration of this appeal, shall extend the time of publication to a period which, in its belief, conserves the interests of all concerned.

Signed on behalf of University of Pittsburgh

Date: _____

Signed on Behalf of A. B. C. COMPANY.

Date: _____

Altogether, the outlook for the establishment of this scheme of industrial research on the basis of permanency seems cheerful. It appears, in so far as one can say, to be a sane, practical scheme, to the advantage of all concerned.

January 6, 1911.

DISCUSSION OF PROFESSOR DUNCAN'S PAPER.

By ALLEN ROGERS.

It has often occurred to me, in observing the methods followed by many of our technical schools and universities, that we are expending a great deal of energy and valuable time on abstract scientific research, which time might be spent to far greater advantage if it were devoted to the solving of some of the many industrial problems which are constantly before us. I have watched with much interest the development of Professor Duncan's plan, and feel that it is a work deserving of great consideration from the manufacturers' standpoint. There is another field, however, which deserves more of our consideration, and that is the field of *practical* industrial chemistry.

By practical industrial chemistry I do not mean instruction given from a textbook, but rather the carrying out of manufacturing operations on a scale sufficiently large to reproduce a fair approximation of the actual working conditions. What our manufacturer most needs is not so much the highly trained analytical or research chemist, but rather the man with sufficient chemical knowledge and practical training to work into such positions as foreman, superintendent, or head of a department; and above all things he should be a man who knows the value of a dollar, and is not afraid of dirt or work.

Ninety per cent. of the foremen, superintendents, and heads of departments in our industries to-day are men of practical experience only, and have no knowledge of the chemical principles underlying the processes over which they have control.

Consequently, when unusual conditions arise, they are at a loss to understand the reason, and unable to suggest a remedy for the same.

With the knowledge of existing conditions, and feeling that there is a demand for men with practical training, the course in applied chemistry at Pratt Institute was inaugurated in September, 1905. Our chief aim is to fit young men for practical work in the various chemical industries.

In the first year of the course in applied chemistry the student is given instruction in general chemistry, qualitative and quantitative analysis, together with a certain amount of physics, mathematics, shop work, and design. In the second year he is given instruction in industrial and organic chemistry supplemented by chemical mathematics, steam and power transmission, shop work and factory design. In our second year analytical instruction we differ radically from other schools in that all of the substances examined are those which are commonly met with in a typical technical laboratory. The following shows some of the materials which are given for analysis: water, gas, fuel, cement, fertilizer, foods, sugar, liquor, alloys, tanning materials, oils, fats, soaps, pigments, paints, boiler compounds, etc., etc.

It is on our industrial laboratory work, however, that we lay especial emphasis, as it is through this method of training that we hope to prepare young men to fill the positions of foremen, superintendents, and heads of departments in the various chemical industries. In order to provide for the practical experience which is necessary in this kind of instruction, we have installed six miniature factories, consisting of a chemical works, a soap factory, a paint works, a dry color and ink works, a dye works, and a tannery.

To meet the demands of a large number of young men who cannot afford the time or money for a four-year course with college requirements, our course has been made but two years in length. At the beginning of the second year one man is appointed as foreman of the chemical works and has four of his classmates as assistants, one acting as oiler. He is told to make an estimate on the manufacture of some chemical, see that his machinery is in perfect condition, and that his factory is kept clean. Before undertaking the preparation he has all materials tested for purity, looks up the market price of the raw and finished products, takes into consideration the wear and tear of machinery, interest on investment, cost of containers, and freight f. o. b. New York. Having determined that the substance can be manufactured at a profit, he then starts its preparation. As soon as one preparation is well under way, a second one is undertaken, as we wish to impress upon our students that an idle factory earns no money and that idle men are sure to develop into strike breeders. By means of this kind of instruction our students learn to handle steam and power, and become familiar with some of the typical forms of apparatus common to all industries. The equipment of the chemical works consists of one 10-gallon steam-jacketed iron kettle, one 10-gallon porcelain-lined, steam-jacketed kettle, one 10-gallon porcelain-lined, steam-jacketed kettle with arbor, one 30-gallon vacuum pan, one vacuum pump, one 3-gallon vacuum copper still, one 5-gallon extractor, one 10-inch centrifugal machine, one vacuum filter, together with drying ovens, and crystallizing tubs.

After one week in the chemical work, the first group goes back to technical analysis, and a second squad takes its place, and so on through the entire class. Squad number one, after spending two weeks in the technical laboratory, is again assigned to the industrial laboratory, but this time to work in the soap factory. The second in line becomes a foreman, and the various processes are conducted in the most practical manner possible.

The equipment of the soap factory consists of a 100-gallon lye tank, a 200-gallon soap kettle, a 100-lb. crutcher four 100-

lb. frames, slabber, cutting machine, chipper, stone roller mill, plodder, and press. Last year our students manufactured 3600 lbs. of toilet soap, all of which found a ready market.

Next in order comes the paint and color works. Here the students are given instruction in the manufacture of pigments and lithographic inks, and become familiar with the process of mixing, grinding, and thinning of ready-mixed paints, together with a knowledge of varnish-making and preparation of enamels. Last year we made and sold 200 gallons of mixed paint. This year, through arrangements with the American Society for Testing Materials, we will grind 160 different kinds of white paints which will be applied to test fences at Roanoke, Va. The amount will be equivalent to about 1000 gallons, the raw materials for which have been furnished by various manufacturers.

The equipment for our dry color works consists of three 5-gallon precipitating tanks, four 10-gallon settling tanks, four 20-gallon sedimentation tanks, a filter press, a ball mill, and a roller mill.

The equipment for the paint factory consists of a 5-gallon paste mixer, a 10-inch iron mill, a kneading machine, two 20-inch water-cooled burr stone mills, and one 20-gallon propeller blade change can mixer.

The work in dyeing is carried along simultaneously with the other work and is conducted by groups of three students. The equipment consists of three 2-gallon steam-jacketed copper kettles, an eight-hole salt bath for silk dyeing and for use with sulphur colors, several dozen dye pots, rods and tripods, a reel, a full-sized jigger, four 15-gallon dye vats, a printing machine, and a steam box.

The instruction in tanning is conducted along the same practical lines as indicated in the other work. Through the affiliation with the National Association of Tanners, however, we have been able to materially add to our equipment during the past year, and have greatly extended the scope of this department. The new installation, which will be completed in a few weeks, will consist of three pits $1\frac{1}{2} \times 5 \times 5$ feet deep for soaking and liming, a paddle for rapid depilation and puering, a fleshing machine, three pits as above for vegetable tannage, two larger pits for layers, an eight-foot drum, three-foot drum, large paddle for chrome tannage, slating table, shaving machine, union splitter, rolling jack, staking machine, buffing machine, and measuring machine. In addition to this equipment we have added a special room for finishing, as well as a room for tacking out and one for drying.

Each student is required to work in all these factories, which takes him into the middle of the Winter term. The remainder of the year his work is confined to that department in which he intends to specialize.

That the kind of training which we are offering is a success is proven by the fact that of the seventy-four graduates and eight special students who have taken the course, there are seventy-eight engaged along chemical lines. Of this number, about seventy-five per cent. are doing practical work. What is more to the point, however, is the fact that of the twenty-three men who finished the course last June, twenty-one were placed before graduation. Eight of these men went to factories where men from the same course were already employed.

Another point which shows the success of this kind of training is evidenced by the fact that when the course was inaugurated in 1905 there were eight men who applied for it, and we had to make up the class from those who had come to the Institute for other lines. Last October, fifty-five men applied for the same course, of which number we could only take thirty-five.

From personal observation, therefore, and from exchange of ideas with many manufacturers all over the country, I am firmly of the opinion that what we most need in this country

is the young man with sufficient chemical knowledge to intelligently supervise our manufacturing operations, and at the same time work in harmony and sympathy with the chemist

By M. C. WHITAKER.

Professor Duncan's plans for the encouragement and development of industrial research opens up an enormous field, and one which will be of immense benefit to the manufacturers. The subjects undertaken should be selected with the greatest care, and should be limited to those branches which can be handled in properly equipped laboratories. Business men may be interested in supporting an industrial research when it can be shown that the laboratory equipment is of a character to offer them superior facilities to those found in their own works laboratories. But it would be a difficult matter to interest a keen business man in an industrial research where the laboratory equipment is no better, or, as in the case of many institutions, even less than may be found in his own works. Plenty of industrial problems may be found, and generous support will be given by industries as fast as it can be demonstrated that qualified men and satisfactory equipment may be enlisted for their solution.

As to the conditions under which chemists have to work in factory laboratories, Professor Duncan's investigation is very interesting and instructive. There are, no doubt, many places where conditions are as bad, or even worse than those described by him. On the other hand, many works laboratories exist where conditions for research and development are far better than those offered by many schools and universities. Some of the industries pay better salaries than the universities; give perfect freedom of working hours; furnish better and more efficient laboratory equipment; provide mechanics, electricians, carpenters, pattern-makers, pipe fitters, plumbers, and all other necessary assistants for the conduct of experimentation on a large scale.

Suppose we consider the position of the works chemist referred to by Professor Duncan from the standpoint of the average works manager. It has been my experience, first, that the chemistry involved in the ordinary manufacturing process is not very profound nor involved, but what there is of it must be sound. Second, that equally important with the chemistry is a knowledge of physics and its application. Third, the principles of thermodynamics are basic in most every manufacturing process at some stage or other. Fourth, a knowledge of the application of mathematics and mechanics is a matter of daily need. Therefore, one of the most important things to be considered in the education of the chemists for manufacturers is the fundamental education.

Equally important and essential to the young chemist in making himself indispensable to the manager is a knowledge of certain other subjects, such as works equipment, works organization, works labor, and works economics.

The margin between a profit and a loss in a chemical manufacture is often very small and no matter how perfectly the chemical reaction may be developed, a poorly equipped works may convert it into a losing venture. Again, a losing chemical process may be, and often is, converted into a dividend-payer by improving and developing the organization for its execution.

Then comes in the question of labor. Of what consequence is the chemical reaction which depends upon labor to make it work, if the chemist does not know how to make a "Dago" work? Now in the education of men to fill the position of works chemists are the schools giving as much care and attention to the training in physics, elements of electricity, thermodynamics, mechanics, and mathematics as they are giving to chemistry? Are the men ever taught the *applications* of these sciences to manufacturing problems with real live factory appliances? Do the students ever realize that the organization factor, the labor factor, the general process economics.

are all equal in importance to their chemical knowledge when it comes to producing the results for which the manager is held responsible and for which he employs the chemist to assist him? The chemist is not discriminated against in the factory. He is employed on the same basis and is favored with the same opportunities as the mechanical, electrical, or civil engineers. To be sure, the field he is expected to cover is larger, but from this very fact it also follows that it is a field of greater possibility. It is a field where failure comes easier to the poorly equipped man, and success is more marked for the properly equipped man.

I think that the factory managers are not altogether to blame for the state of affairs Dr. Duncan has described. The chemists are not altogether to blame either. The education of the men to solve the problems of chemical manufacture is a great undertaking, and one which is not to be considered on the same basis as in other engineering fields.

The subject is broader in its scope, the education must be broader, must consume more time than at present, and leave less for the employer to complete. When this phase of the subject is appreciated and the proper remedy applied, the chemist will assume a position of indispensable importance in every factory. The question of his relation to the pay-roll, hours of labor, security of position, and share of profits will solve itself on the only secure basis for any adjustment—*efficiency*.

By DR. L. H. BAEKELAND.

One of the main reasons why the work of the chemist is not properly understood nor properly appreciated is that the average public, even including educated men who are not chemists themselves, is not in a position to grasp the scope and the purposes of chemical investigation. The man of average intelligence can easily understand a mechanical proposition involving the work of the engineer, but it requires chemical knowledge, besides intelligence, to have some understanding of chemical problems and their difficulties. The average man has only the haziest conceptions of this subject.

Chemical research work, at its very best, is slow in practical results, and what is still worse, the real visible difficulties begin only after the initial research work is over, and the subject is to be reduced to practice. Therefore, to an uninformed person, the value of all the preliminary painstaking research work is not very apparent.

Ramsay stated that "The country which is in advance of the world in chemistry will also be foremost in wealth and general prosperity." It is a great advantage for this country to have at last a man like Professor Duncan, who is able to initiate the public at large into the mysteries and the scope of chemical problems. The fact that he has succeeded in treating these subjects in a popular and brilliant style increases its merit.

Research in industrial chemistry involves work of no less high order and no less difficulties than that required for purely scientific investigation. In fact, the man engaged in purely theoretical work has a great advantage over the industrial chemist because he has to take into consideration the cost of production, the market conditions, and the factor of superiority of quality. If the theoretical investigation of the subject becomes too difficult, or does not bring in results, or does not ease him, he does not have to pass sleepless nights over it, but he can simply drop it then and there, and quietly select some other line of work more to his liking, and carry it out according to his own fancies and without submitting himself to the drastic criticisms of the consumer or the market at large.

The question of suitable compensation for research chemists was touched upon this evening. This is a difficult matter to discuss, and depends on many factors. It is quite natural that a chemist, who receives a fair salary from his employer for doing chemical research work, should assign to his employer

any patents he takes out, the subject of which is the direct or indirect result of the opportunities thus furnished by his employers and the study of which is at the latter's expense. Furthermore, an invention or an improvement is often made piece-meal and is the work of several collaborators. Sometimes it becomes very difficult to decide to whom belongs the merit of the final practical results. While I believe that it is fair for an employer to claim the ownership of any invention or work performed by his chemists while they are in his service, it may be to the better interest of the employer to find a suitable way to stimulate initiative by recompensing any valuable work, either by an increase of salary, or better, by some small, but fair participation in the benefits of the undertaking.

An arrangement which simply compels the chemist to forfeit all claims on improvements introduced by him, and which, at the same time, offers only an insufficient salary, is simply antagonistic to the interests of the employer, and gives the chemist no inducement whatever to exercise his initiative or best endeavors.

It is difficult or inexpedient to embody all this in a contract, but the employer may find it to his advantage to convince his research chemists that their successful work is to be taken as a basis for advancement.

Too few chemical inventors realize the enormous distance which lies between a laboratory conception and its successful application to practice. Many problems which are solved in the laboratory after great effort often require years of painstaking work, not to speak of immense financial sacrifices, before they are acceptable in current practice and become a basis for a paying commercial operation. By the latter I do not mean, of course, the so-called "rake-off" of promoters, who frequently begin by smothering a good thing under too heavy charges.

And now a word as to the value of the patents. If you do not patent your inventions and if you prefer to work them secretly, you take the risk of having your work interfered with at any time, not only by others copying it, but by somebody else taking out very disturbing patents, which afterwards may cost you much time and money in litigation.

If, on the other hand, you are protected by patents, but do not possess the financial means to defend your rights against infringers, some unscrupulous parties may harass you on the chance that you lack financial support for defending your rights.

In the United States we have an excellent patent law, which is very broad and very fair to the inventor, but we have a most absurd and wretched system for settling infringement suits. Patent litigation has become a huge force in this country, and at the same time, a very expensive pastime for both patentees and infringers. It gives a splendid chance for unscrupulous lawyers and experts to reap enormous fees, and gives little satisfaction to the litigants. This state of affairs arose from the day when the Supreme Court could no longer find the time to act as a court of appeals, and had to leave the whole matter to the different Circuit Courts, who often reach entirely contradictory decisions.

Let us hope, therefore, that the long pending bill for a Patent Court of Appeals may finally become a law and put a stop to this utterly nonsensical condition of affairs. Later on, such a court of appeals will naturally be led to discourage the present prevailing dilatory system of taking testimony in patent cases, and thus put a stop to a situation which has become well-nigh intolerable, and which conflicts greatly with the interests of our industries.¹

PROFESSOR DUNCAN'S CLOSE OF THE DISCUSSION.

Dr. Baekeland's reference to my interpretative work in science is deeply appreciated by me. This work of scientific exegesis, if I may so call it, is not easy.

¹ See "Symposium on Patents," THIS JOURNAL, April, 1909.

I have listened with interest to Professor Rogers' presentation of his scheme of instruction. It represents a sensible, coherent, practical scheme of service, particularly apposite to the ideals of the type of institution to which he belongs.

It does strike me, however, that this work might be carried out with much less expense to the institution and, possibly, with just as large an efficiency, by arranging coöperative relations with neighboring industrial plants, by which the student might alternate in his time between the plant and the laboratory.

It is, however, certainly a fact that next to the need of real scientific research in the factory organization, there lies the necessity of foremen and superintendents trained into an intelligent appreciation and knowledge of the practical bearing and utility of science. Who can tell how much ruin has been wrought to applied science through the ignorant prejudice and stupid opposition of factory foremen?

But it is to the application of Professor Rogers' ideas to the university type of instruction that I should make particular objection.

That is, in fact, what seems to be the trouble with many of the departments of so-called industrial chemistry in the universities. They teach a student to make a little paint, a little dye, a little soap, a little glass, etc., and thus after having taken him away from some good courses in physical, organic or analytic chemistry, they turn him loose as an industrial chemist. In other words, in teaching him industrial chemistry, most inadequately and inefficiently, they teach him *multa not multum*. As I have said before,¹ it is not the function of a university to limit men but to free them to the exercise of their maximum powers. In a trade school men enter already limited.

This brings me to Professor Whitaker's remarks. It is undoubtedly true, as he says, that the successful conduct of my work under these industrial fellowships depends upon adequate facilities of laboratory equipment. But it is just as true that success depends upon the maintenance of a certain spirit favorable to research which is seldom found in the "common or garden" type of factory laboratory. Again, it depends upon our power to obtain, rapidly and accurately, exclusive information, and, still again, it depends upon the sympathetic coöperation in each individual case of the university with the factory. Fundamentally, success depends upon the men chosen. In coming to me they are fully informed that they are not entering upon a work intended for old ladies or little children.

Professor Whitaker's statements that there do exist in America good factory laboratories for research are of course perfectly true and I have an uneasy feeling that in the statements made in the body of my address I did not sufficiently differentiate the good examples that we have. We undoubtedly have in this country factory laboratories the peer of any that exist. They are, however, connected with just a few large organizations and, numerically, are unable to leaven the whole lump.

Professor Whitaker's ideas as to the education of a chemical engineer are ideal, though he seems to be referring to the creation of an executive works chemist rather than to a true industrial researcher. As for the latter, instead of needing chemistry "not very profound but sound," my experience is that he needs all the contemporary chemistry that God has given him power to absorb.

The education of the executive works chemist along the lines suggested by Professor Whitaker while ideal would, it seems to me, take twenty years to realize. Certainly it cannot be accomplished in a period of gestation of four years. The fact of the matter is that on leaving the university the industrial chemist's education is of simple necessity just beginning. Personally, I believe that the solution of the university training of the industrial chemist lies in the scheme of industrial fellowships,

the development of which I have indicated above. I was late in understanding this, but it is obvious since going to Pittsburgh that the building when erected will be unable to accommodate the demands that will be made upon it.

On the possession of this building there will be at least fifty chemists highly trained and specialized for sustained research in various industries. These fifty men, through their instructional duties provided for in the agreements, will constitute a unique staff for the teaching of undergraduates or graduates for service in specific industries and even for specific organizations.

This seems to me, without attempting to minimize the splendid methods of Professor Whitaker or Dr. Rogers, the suitable solution of the problem of teaching industrial chemistry in the universities. It removes the inconsistency of trying to teach general industrial chemistry to young men at the expense of their chemical and cultural education.

CHEMISTRY AND THE ENGINEER.¹

By GEORGE BORROWMAN.

As a factor in engineering, chemical knowledge has had, in the past, comparatively little significance for practising members of the profession. To-day it is rendering a service that is recognized as of great and increasing importance and in some branches of work, second only to mathematics. This is not charging the pioneers with stupidity. The change is but one evidence of the wonderful growth of engineering activity.

The early gold seeker refused to take seriously a knowledge of geology and metallurgy. These subjects were "frills." All he needed was an eye for gold, a pan, a little mercury and water. But the time for gathering surface nuggets passed and to-day the vast underground achievements and complex ore treatments testify to the increased knowledge and equipment of the modern mining engineer.

Civil, mechanical and electrical engineers are no longer in the day of surface nuggets. Human activity, the history of which presents a growth from the simple to the complex, is manifested in no small degree by the development of these three branches of the profession. The farther we get from primitive conditions, the less easy it becomes to satisfy our physical needs. The obvious applications of natural resources no longer suffice and as a consequence, new methods of utilizing energy, new artificial materials are devised. This means increased knowledge, a study of the more intimate relations between forces and substances. In short, physics and chemistry become of vital importance. Thus, much that was yesterday considered extraneous is counted necessary in the widened vision of to-day.

The chemical composition of the materials of engineering is being extensively studied, throwing light on such questions as: the effect of phosphorus and sulphur on high-speed tool steel; the influence of aluminates on the setting and strength of cements; the electrical conductivity of alloys, etc.; the changes brought about in materials exposed to certain environments. Through chemical investigations we are learning more about the corrosion of iron embedded in concrete; the deteriora-

¹ THIS JOURNAL, Aug., 1909.

¹ An address delivered before the Nebraska Section of the A. I. E. E., December 8, 1910.

tion of steel work exposed to locomotive gases; the effect of sea water upon concrete; the efficiency of the many insulating materials under various conditions and numerous other problems of like engineering importance. As a result of all this, engineers are drawing up specifications and designs more intelligently and manufacturers are enabled to meet requirements with more precision.

So much may be said for chemistry and engineering in general. This being a body of electrical engineers you are of course particularly interested in the application of this subject to your work.

In my opinion, chemistry is of greater importance to you than to the other branches of engineering. It has a peculiar significance that involves much more than the chemistry of materials, due in part to the relation between chemical and electrical energy, if indeed they are not identical. Many chemical changes can be assisted by electricity and some can be produced only by means of this agent. These reactions are grouped under the name of electrochemistry, with which, no doubt, most of you have at least a laboratory acquaintance. I question, however, whether you are aware of the extent to which this work has been recognized by the industrial world and of the present importance of electrochemistry in the utilization of power.

Manufacturing, as well as other activities, is becoming more intensive. Natural processes are, in many cases, inadequate for present-day demands and as a result electrochemical reactions, on a large scale, are rapidly supplanting the older, slower, straight chemical procedures. In fact an authority in electrical matters informed me recently that this branch of manufacturing is already a large consumer of power and will probably be, in the near future, the largest consumer, if such is not at present a fact. This being the direction of electrical development, the importance of chemistry to you is self-evident and warrants serious consideration.

In support of these statements it will not be necessary to go into an exhaustive account of the growth of electrochemistry and detailed descriptions of processes. I desire to present, however, a few descriptions and historical facts, aided by a little demonstration, which will suffice to give you some conception of the work.

Electrical energy is susceptible of two important methods of application in chemical work—electrolytic action on solution and utilization of thermal effects. The first process, known as electrolysis, is an old and familiar one in principle at least. When a compound substance in solution is subjected to the electric current under proper conditions, it is decomposed, the electropositive constituent being deposited at the negative electrode and the electronegative at the positive terminal. Perhaps the simplest example of this action is the decomposition of acidified water as shown by the Hoffman apparatus. Hydrogen collects in one arm, oxygen in the other. This is not merely an interesting lecture demonstration but a method used on a large scale in manufacturing these gases for

commercial purposes. There is such a plant at Omaha.

Another much more important and significant application of this principle is the electro-manufacture of caustic soda. The older chemical process is long and tedious. Common salt is first treated with sulphuric acid to produce sodium sulphate. The sulphate is next heated with carbon to make sulphide of soda, which in turn is converted to carbonate by calcium carbonate. Finally the sodium carbonate is treated with lime water, yielding a solution of caustic soda. By the electrolytic method caustic soda is obtained from common salt by one step. When the salt solution is subjected to the current it decomposes, as in the case of the water, into its constituents chlorine and sodium, the former escaping as a gas at the positive electrode and the latter tending to separate at the negative electrode. Metallic sodium, however, does not appear as such but reacts with the water, liberating hydrogen and forming caustic soda. By proper arrangements the chlorine gas is conducted into lime to make bleaching-powder.

As compared with the former, chemical process, this is simplicity itself and seems certain to displace the older method entirely. It is rather difficult to get complete details of these plants because the precise methods employed are kept secret. The most important process used in this country is probably the Castner-Kellner. The plant at Niagara owned by the Mathieson Alkali Company was 2000 h. p. in 1900, and the output was about ten tons of caustic soda and twenty-four tons of bleaching-powder per twenty-four hours. The current efficiency was high, about 85 per cent.; the voltage required, 3.5; the energy efficiency 55-59 per cent. These facts have been published by Bertram Blount.

In the production of metals also, electrolysis is doing a wonderful work. The price of some, such as aluminum, would be prohibitive were it not for cheap electro-processes. Others, as magnesium, cannot be produced commercially in any other way. In the refining of metals, too, the electrolytic principle is used, affording metals of a degree of purity impossible to obtain otherwise.

The utilization of the thermal effects of electrical energy involves two very different methods. In one, use is made of the plain heating effects of the electric furnace; in the other, high tension arc discharges. The furnace heated by electricity owes its place in manufacturing to the high temperatures attainable and to efficiency. A number of high temperature reactions, hitherto unknown, at least industrially, take place in the electric furnace and have resulted in the production of several valuable substances. For example, carbon and lime have no attraction for each other at ordinary temperatures. In the electric furnace, at 3300° C., they form calcium carbide, so important as a source of acetylene gas. Successful plants produce about 4 kilos per h. p. per twenty-four hours. Carbon and sand are made to combine at high temperature to form the well-known abrasive, carborundum. The power needed for this product is stated by

Blount as 8.6 kilowatt hours per kilogram. Artificial graphite is another electric furnace product, made by heating amorphous carbon to a high temperature. For the two latter substances we are indebted to Dr. E. G. Acheson.

In the employment of the electric arc for chemical manufacture we have the crowning achievement in electrochemical work—the fixation of atmospheric nitrogen and the synthesis of nitrates. The importance of this warrants my dwelling on it somewhat in detail.

In the first place, combined nitrogen is absolutely essential to life. Nitrogen compounds are found in protoplasm, that part of the cell where the life process goes on. Only a few organisms, certain bacteria, are capable of taking free nitrogen and combining it. Consequently the higher forms are dependent upon the lower for nitrogen compounds. This source of supply is, in this day of intensive agriculture, inadequate and hence the use of fertilizers containing nitrogen. Compounds suitable for this purpose are found native in but few places on the globe. They are chiefly nitrates of sodium and potassium and occur most abundantly in South America where the Chili nitrate kings are waxing wealthy on their monopoly. It requires no great foresight to see that these deposits would in time become exhausted and the problem of artificial nitrates began to attract scientific attention years ago. After much study and many experimental failures, the puzzle was solved, thanks to electrochemistry.

It was known for a long time that electric sparks in the air caused small quantities of nitrogen and oxygen to combine. This was the starting point, and experiments were directed to increase the efficiency of the reaction. At the arc temperature of 3000°C . considerable oxide of nitrogen will be formed but the decomposition at high temperatures is great also. The problem of securing increased yield was largely one of sudden cooling of the gases after leaving the arc. One of the first devices, from which much was expected, involved many arcs of small energy content. The arrangement was too complex and was finally given up.

About the beginning of the last decade the matter was again tried out by two Norwegian inventors, Birkeland and Eyde, who succeeded in devising a workable plant in use to-day. They employ a strong current and large arc which is drawn from side to side by means of an electro-magnet. The vibrations of the arc permit contact with a large volume of air. The immediate product of the arc is nitric oxide, part of which oxidizes to nitrogen peroxide on coming in contact with the air. The mixed gases are washed by water, forming a solution of nitrous acid and nitric acid. Nitrates are made from the acid by treating with soda or lime. The process is entirely successful and at Notodden, Norway, there is a factory using 30,000 h. p.

It remained for the Germans, however, to simplify the method still further. Dr. Schoenherr, to whom I am indebted for some of the details of this industry,

employed by the Badische Anilin and Soda-Fabrik, was largely responsible for this advancement. His study of the problem resulted in discovering a method of using a stationary, continuous arc acting on a current of air blown spirally around it. His company has an experimental plant at Christiansand, Norway. They have 1300 kw. feeding three furnaces with 600 h. p. each, under a tension of 4200 volts. The arc produced is about 5 meters long. The furnace, according to Dr. Schoenherr, consists essentially of an iron pipe in upright position. In the lower end is an insulated electrode. The upper end is water-cooled. Near the lower end are openings to permit air to be blown in tangentially. A short arc is struck between the electrode and the side of the pipe. The air current then carries one end of the arc up the side of the tube until it terminates on the upper, water-cooled end. The result is a long flaming arc surrounded by a whirling current of air. Instead of forcing cold air directly into the arc, it is given a preliminary heating by allowing it to enter an outer pipe and traverse the length of the arc tube to the tangential openings.

The gases coming from the arc are cooled to about 1200°C . before leaving the tube. As the temperature sinks lower the nitric oxide takes up oxygen from the air and becomes peroxide. The gases are absorbed by milk of lime forming calcium nitrate and nitrite which, according to several authorities, is quite as suitable for use as a fertilizer as the straight nitrate.

This, in brief, is the history and present status of the artificial nitrate industry, which is destined to become one of the chief factors in future civilization. The whole present electrochemical activity is, to my mind, the mere beginning of a work pregnant with possibilities for the electrochemical technologist. Much of the work requires great expenditure of power which must therefore be cheap, but this should be no deterrent since but a small fraction of the world's water-power is now utilized.

In closing, the facts seem to warrant the conclusion that in present-day general engineering, a knowledge of the chemistry of materials is of considerable service, and that the demands of the future in this respect will be probably still more urgent; also that in the electrical department, there is rapidly opening up a field of activity where engineers with special chemical training will find many opportunities for the exercise of chemical and mechanical ingenuity.

THE THEORETICAL BASIS FOR THE USE OF COMMERCIAL FERTILIZERS.¹

By FRANK K. CAMERON.

The recent trend of events in this country makes especially important the problem of fertilizers, which must be met wisely if efficient use is to be made of that great national asset, the soil. Much is being brought to light regarding the sources of supply, the results of field tests, etc. It is the purpose of this paper to state the case in a way which, it is believed,

¹ Abstract of remarks made before the Division of Fertilizer Chemists, at the Minneapolis Meeting. Published by permission of the Secretary of Agriculture.

makes clearer the problem, the method of attack available to the scientist, and the correct attitude of the fertilizer producer.

From an agricultural standpoint, the soil may be defined as that portion of the land surface adapted to the support and growth of a crop plant or plants. It is a system of many components, mineral and organic, and contains living organisms. The material remnants and detritus of nearly if not all activities on the solid portion of the earth's surface find their way to the soil, and by various transporting agencies, especially water and wind, are carried from soil to soil.

Not only the number but the relative proportions of the various components vary quite widely in different soils. Moreover, every component of the soil is continually involved in processes of change. Therefore each soil is a dynamic system, with a complex summation of properties;¹ consequently it is highly individuated; no two soils can be expected to be exactly alike, nor any one particular soil to remain just the same from time to time, either in crop-producing power or response to cultural methods. Each soil must be regarded as a distinct entity, with its own properties; but these properties are continually being modified as a result of activities within the soil as well as by natural and artificial agencies from without.

With these considerations in mind the theory of soil management or control can be easily formulated. For further simplicity a mathematical terminology can be employed, it being clearly understood, however, that no mathematical ideas are implied other than those explicitly stated.

Crop production (C) is dependent upon: the biological peculiarities of the plant or crop (P); the amount and distribution of the rainfall (r) and the sun's energy (s); the properties of the soil, physical (p), chemical (c) and biological (b); and upon other factors, the number being yet uncertain but probably large. Besides these natural factors, a cultivated crop is dependent upon artificial methods of control which fall conveniently into the three classes, tillage methods (T), crop rotations (R), and fertilizers (F). This dependence may be expressed as follows:

$$C = f(P, r, s, p, c, b, \dots, T, R, F)$$

What the nature of this function may be, no one yet knows. It has generally been assumed that it is simple, and by many investigators, that it is a linear function. It is reasonably certain, however, that it is quite complex, and certainly it is not linear as is shown by the accumulated results of plot experiments.

Two methods of attacking this function suggest themselves. Suppose the different factors are independent variables. Then, obviously, the proper experimental procedure is to keep all but one constant, and varying that one, to measure the effect by the crop produced. This is the method which has generally been attempted by agricultural investigators, as in the popular plot tests for fertilizers and in

greenhouse cultures. An enormous amount of data has been accumulated, but the results have been disappointing. If the assumption of independent variables were valid, it should be comparatively easy to determine the nature of the function; and if, in addition, the function were linear, fertilizer effects, for instance, should be additive. The evidence shows fertilizer effects to be generally (though not always) cumulative, *i. e.*, three constituents are more effective than two, and two more effective than one.² But the effects are *not* additive, the effects of a mixed fertilizer being sometimes greater, more often less, than the sum of the effects produced by each component separately. As stated above, the nature of the function is yet undetermined.

Consideration of the large mass of experimental evidence that has been accumulated in the field and laboratory leads inevitably to the conclusion that all the factors in crop production are dependent variables. Altering the chemical properties (c) for instance always affects the physical properties, the biological properties, the distribution of moisture, etc. Tillage obviously changes the physical properties of the soil; it necessarily affects the bacteria and other biological factors in the soil, the chemistry, organic as well as inorganic, presumably the functioning of the plant, etc. Concrete example is furnished by the addition of potassium carbonate (F) to a loam soil. The factor c was increased, but the soil was deflocculated and somewhat puddled, p being decreased; the growth of desirable bacteria was inhibited, with presumably an increase in undesirable kinds, thus decreasing b ; and without attempting to follow the effects on the other factors, it may be said that the summation of these several results as expressed in crop yield (C) was a decrease.

Recognition that the variables in the function representing crop production are dependent suggests the second method of attack, namely, to attempt the substitution of each variable in terms of some one.² Experimentally this is difficult and perhaps not actually susceptible of complete accomplishment. It is practicable, however, to do much in this direction. Clearly, a mere measurement of crop production can not in itself furnish much information. If the plot experiments with fertilizers of the future are to be of any real assistance, observations must be made upon the physical and biological properties of the soil, at least throughout the growing season. Not only the yield of crop, but the character of the yield, the particular life history of the crop must be recorded. More important at the present time perhaps is the determination of the kind and degree of the changes produced in different variables by the changes in any one of them. This mode of procedure is absolutely essential if a rational system of soil management is to be developed.

¹ Bureau of Soils, U. S. Dept. Agriculture *Bulls.* 58, 62, 64, 65, 66, 67.

² It hardly seems necessary to state that this does *not* imply that, in practice, fertilizers can take the place, or perform the functions of tillage or crop rotation. It can not be too strongly emphasized that good farming requires the employment of all three methods of control.

¹ THIS JOURNAL, 1, 806 (1909); *J. Phys. Chem.*, 14, 320 and 393 (1910).

Confining attention to that artificial factor most easily controlled by man, several important considerations must be noted.

There is now existing a considerable mass of experimental evidence supporting the general view outlined above. It is known that definite organic substances are present in soils,¹ some of which are toxic to various plants, and that the addition of fertilizer salts modifies the toxicity or inhibiting influence, and it has been shown that these modifying influences are specific. It is known that oxidizing processes on the one hand and reductions on the other, produced by organic substances, enzymes, bacteria, and probably inorganic substances, are normally taking place in every soil which more or less affect the adaptability of that particular soil for different crops; and it has been shown that these oxidations and reductions are markedly affected by the addition of inorganic salts in commercial fertilizers. And so far as the available evidence goes, again the activities of these salts are specific.²

It has been shown that the activities of bacteria and lower plant forms in the soil are much influenced by the salts in commercial fertilizers, and these activities are very potent in determining the growth of higher crop plants. The mechanical properties of the soil and the physical properties of the soil solution, as in its density, its movement through the soil, and other phenomena of importance to crop production, are affected by soluble salts. The absorptive power of the soil towards the different salts and their various constituents is now recognized as of very great importance in determining the relationships to crop yield. The addition of a salt may sometimes influence their absorptions, as in the case of a soluble nitrate lessening the absorption of phosphoric acid,³ with marked result in the crop. And it has been shown that the addition of salts has a measurable influence on the optimum water content, and the many physical properties of the soil dependent on the water content.⁴ It is well known that flocculation or deflocculation is affected by exceedingly small proportions of salts; thus "crumbing" of the soil and its tilth can be markedly affected by the addition of fertilizers.⁵ The hitherto popular notion that these physical effects are of minor importance is due mainly to the fact that investigators have not known what observations were necessary nor how to measure them. But without going into detail here, it may be said that the physical effects of fertilizers on the soil are now known to have an importance for crop production which can no longer be slighted. Numerous water culture and other experiments leave no doubt that fertilizers directly affect the functioning of the plant, as well as influencing it through their effects on the soil, and this fact needs no further exposition here.

While the lines of investigation covering the various

kinds of effects produced by the constituents of commercial fertilizers are as yet hardly more than initiated, they have nevertheless progressed sufficiently to leave no manner of doubt that fertilizers in some way and to some extent influence each and every known factor affecting crop production. Obviously no simple explanation of the value of fertilizers can be correct, but all the possible effects on the various factors influencing crop production must be considered. Consequently no simple procedure for examining soils, such as the analysis of an acid extract, can in itself be expected to furnish a satisfactory idea of the productivity of a soil, or its fertilizer requirements; a much more comprehensive analysis of the soil conditions is necessary together with a knowledge of the crop factors; and for an intelligent utilization of the soil, to develop its best commercial efficacy, there must also be known the economic factors affecting the growing, shipping, and marketing of the crop or crops. These latter factors, while often regarded as outside the province of the soil expert, can not be disregarded in the larger considerations of the subject.

One economic consideration suggested by this view of fertilizers has hitherto escaped consideration, although of enormous importance to this country. The annual expenditure for fertilizers in the United States is probably not far from \$120,000,000, of which it is safe to say 80 per cent. is spent in the South Atlantic States and less than 5 per cent. is spent in the trans-Mississippi States. And this condition of the fertilizer industry is accepted with apparent placidity, under the influence of the prevalent notion that fertilizers are of value only for the mineral plant foods they contain, and the further idea that the soils of the eastern states and especially of the southern states are "worn out" and depleted of available plant food.¹ The western states, on the contrary, because they have less recently developed are supposed to be still rich in plant foods, and this notion is supported, speaking generally, by intense local pride, denying the value of fertilizers for fear it will appear an admission that the local soils are wearing out and becoming less productive than those of neighboring areas. Yet the production of our staple crops per acre is higher in the older than in the newer states. It is a widely accepted opinion in Europe that fertilizers pay best on the "richer lands," and this appears to be the view of those consummate farmers of the Occident, the Japanese, who have a popular saying to the effect that the way to ruin a farmer is to put him on virgin land.

There is no real evidence that *per se* the soils of the eastern states are inferior in crop-producing ability to the soils of the more recently settled west, but if it were true, the idea of complex fertilizer effects, and the nature of the function representing crop production, would lead to the conclusion which has strong support in the more highly developed agriculture of Europe and the Occident, namely, that fer-

¹ Bureau of Soils, U. S. Dept. Agriculture, *Bull.* 53.

² *Ibid.*, *Bull.* 73.

³ Unpublished experiments by H. E. Patten.

⁴ Unpublished experiments by R. O. E. Davis. See also *Bull.* 50, Bureau of Soils, U. S. Dept. Agriculture.

⁵ *J. Frank. Inst.*, 169, 421-38; 170, 46-57 (1910).

¹ "Regarding the Supply of Mineral Plant Nutrients," see *J. Phys. Chem.*, 14, 356 (1910).

tilizers should prove more profitable on the better soils. With the rapid occupation of all available land, rise in land values, and the necessary introduction of more intensive methods of cultivation, the time is at hand if it has not already come, when the western agricultural states should be the greatest consumers of commercial fertilizers. That this important development should much longer be retarded if not blocked by popular adherence to an unscientific and antiquated theory is inconceivable, yet one finds not only some agricultural investigators, but even some fertilizer chemists still clinging to it.

The difficulty which seems to have the most significance for the rigid advocates of the older theory of fertilizer action is the supposed fact that only those fertilizers are effective which contain potassium, phosphorus (as phosphates), or nitrogen, and the question is seriously asked: why, if these ideas are correct, cannot sodium chloride be used in place of the more expensive potassium salts? The answer however is quite clear. It is no more reasonable to expect sodium chloride to produce the same effects that potassium chloride does than it is to expect these same effects from a soluble phosphate. Each salt has its own specific properties and must be expected to produce effects which differ in kind as well as degree; and this quite apart from the facts that there is some evidence favoring the view that sodium can partially at least replace potassium in the mechanics of plant metabolism,¹ and that it is recognized by every one that under the conditions of plant growth as we know them, the presence of potassium in the cell sap is essential to plant growth and the presence of sodium is not. As a matter of further fact, sodium chloride has sometimes been used as a fertilizer and in general with about the same kind of success that has followed the use of other soluble salts, namely, in a majority of cases there was a more or less satisfactory increase of crop production. Whether or not sodium chloride should have a place among the standard fertilizer salts is by no means a settled question, and time and further experience with it are needed. It has the essential requirements of a commercial fertilizer, in that it affects plant growth, under proper conditions favorably, it is obtainable from a large and permanent source of supply, and is cheap. Moreover, it is about the only substance meeting these requirements that is not generally in use as a fertilizer. If future experience should show that it is not a useful soil amendment it will certainly be for other reasons than that it does not contain a recognized plant food.

In this paper, it is pointed out that:

1. Crop production is the result of many factors, natural and artificial, and these factors are all mutually dependent.
2. No simple theory of fertilizer action can satisfactorily account for the known facts.
3. With intensive methods of cultivation, fertilizers are effective on all kinds of soils, and are the more efficient on the naturally better soils.

¹ See, for instance, the work of Wheeler and his colleagues. *Report of the State Experiment Station of Rhode Island*, 1894 to 1909.

4. Other materials than those containing the traditional plant foods may yet become valuable fertilizers, if they satisfy commercial requirements.

BLEACHING WITH SODIUM PERBORATE.

By J. MERRITT MATTHEWS, Ph.D.

Though sodium perborate, as well as other salts of perboric acid, have been known to the chemist for some time, it has only been within the past year or two that their use has been put forward for purposes of bleaching. The chief salt which is available for this purpose is sodium perborate, though magnesium perborate has also been employed. Sodium perborate is a substance similar to sodium peroxide in that it has a considerable amount of loosely combined oxygen, which under proper circumstances is readily liberated from combination in the nascent state, and thus becomes available for use in bleaching.

Sodium perborate has been principally exploited in Germany during the past few years, where its use for various purposes of bleaching has been the subject of quite a number of patents, though it is to be doubted whether these patents possess any commercial value. From Germany the use of sodium perborate spread to England, where it has been the subject principally of advertisements rather than entering into any practical use. During the past year, sodium perborate has appeared in the American market, and we believe it is also manufactured in this country at the present time.

Sodium perborate is prepared from sodium peroxide and boric acid. As compounds derived from boron are all more or less expensive commercially as compared with compounds of sodium alone, it is reasonable to expect that sodium perborate would be more expensive than sodium peroxide when based on an equivalence of available oxygen. Furthermore, sodium perborate even in the pure condition, contains only 10.4 per cent. of active oxygen, whereas sodium peroxide contains about 20 per cent., or practically twice as much in the same amount of chemical.

In its general application to purposes of bleaching textiles, sodium perborate is very similar to sodium peroxide or hydrogen peroxide. In fact, the various per-oxygen chemical compounds which have from time to time been suggested as capable bleaching agents, such as perborates, percarbonates, and persulphates, all depend in the final resort for their bleaching activity on the fact that they readily furnish a solution of hydrogen peroxide when dissolved in water, or when their solutions are treated with a suitable acid. Therefore the bleaching process with all these reagents comes down to a question of bleaching with hydrogen peroxide. In the consideration of this question, the chief factors to be discussed are the comparative amounts of hydrogen peroxide formed from equal quantities of the different compounds, the relative cost of the hydrogen peroxide thus produced, and whether the decomposition of the product brings into the solution other ingredients which may hinder the activity of the hydrogen peroxide in its bleaching efficiency.

Hydrogen peroxide, itself, as it appears on the market is simply a solution of this reagent in water with usually a small amount of acetanilide, phosphoric acid, or other suitable preservative. The solution is quite dilute, usually containing about three per cent. of hydrogen peroxide, as stronger solutions are very unstable and cannot be kept for any length of time. The amount of preservative is very minute, its only purpose is to retard the decomposition of the hydrogen peroxide, and in its character and amount is without significance as far as its influence on bleaching is concerned. Sodium peroxide is a solid substance, and when dissolved in water gives rise to a solution of hydrogen peroxide and caustic soda. The latter has to be neutralized with sulphuric acid in the preparation of the bleaching bath; so this bath then consists of a dilute solution of hydrogen peroxide containing a relatively large amount of dissolved sodium sulphate or Glauber's salt. This latter substance is of a neutral character as far as the bleaching effect goes, but its presence in the bath in such large amounts as compared with the amount of actual hydrogen peroxide seems to lower the efficiency of the bleaching action of the latter. Sodium peroxide, however, on account of the high percentage of per-oxygen in its chemical composition, is a comparatively cheap source for the preparation of solutions of hydrogen peroxide, and is also much more stable. Owing to these facts, sodium peroxide has been largely employed in bleaching for the preparation of solutions of hydrogen peroxide.

Sodium perborate is even more stable in its nature than sodium peroxide, and it was principally on this account that it attracted attention for purposes of bleaching. Whereas sodium peroxide decomposes with violent rapidity when dissolved in cold water, sodium perborate requires to be dissolved in hot water in order that it be decomposed completely, and the resulting products are hydrogen peroxide, caustic soda, and borax. It may be probable, however, that some or all of the borax may exist in the solution as metaborate of sodium. The treatment of this solution with sulphuric acid for the purpose of neutralizing the caustic soda is not absolutely essential in the case of bleaching cotton materials, and the bleaching bath may be employed at an elevated temperature. In cases where the wool fiber is to be bleached, however, it would be very essential to neutralize the caustic soda with sulphuric acid, in order to avoid the destructive action of the caustic alkali on the wool. The same would also be the case in the bleaching of silk materials.

It has not been demonstrated that bleaching baths prepared from sodium perborate are as efficient as the bath containing pure hydrogen peroxide alone, and at the present market prices, solutions prepared from sodium perborate show a relatively higher cost for the same amount of active bleaching agent. In this respect, in fact, sodium perborate is expensive out of all proportion when compared with sodium peroxide. The exact utility of sodium perborate,

then, for purposes of general textile bleaching is hard to discover. Its only advantage that is at all apparent in this connection is that the bleaching solution may be employed at relatively high temperatures, and thus can be used directly in a kier; but whether it is an advantage to bleach at a high temperature or not is a question. It would usually be considered that bleaching carried out at as low a temperature as possible would be more conducive to the preservative of the good qualities of the articles being treated.

Under the present conditions it would seem that the only feasible application in view for sodium perborate would be in the laundries, where it could be efficiently employed in place of the chlorine bleaching agents at present used, and which are so exceedingly destructive of our collars and shirts as well as all our household cotton goods which perforce are required to make the trip to the laundry a few times. The modern laundry employs, in a reckless manner, bleaching agents for the purpose of whitening up the goods instead of hanging them out on the line and thus exposing them to the mild and effective bleaching action of the sun and atmosphere. The laundries are coming to be large users of either solutions of chloride of lime or electrolytically prepared solutions of sodium hypochlorite for bleaching purposes. Both of these solutions have practically the same effect in the rapid deterioration of cotton materials, especially when used by the more or less haphazard methods of the average laundry, and by persons who do not fully realize the destructive effect of chlorine and acid compounds on cotton. Many laundries fondly imagine that when they are employing an electrolytic cell for the preparation of their bleach liquor from salt water, they are only using the salt water itself for the whitening of the goods, and attribute the bleaching effect to some occult cause in the electric current. In reality, the electric current has nothing at all to do with the bleaching effect; the current is simply used for the purpose of decomposing the salt solution in order to form a solution of sodium hypochlorite, and this latter substance is as violent in its chemical action as a corresponding solution of chloride of lime. Again, it is highly probable that many laundries will attempt to apply their bleaching liquors in hot solutions, which, of course, is ruinous to the cotton material so unfortunate as to meet with this treatment. Again, if the laundry attempts to whiten materials containing wool or silk fiber in this manner with chlorine compounds, the animal fiber will naturally be destroyed. Merino underwear or half-silk underwear is often rendered unfit for further use by such treatment at the laundry.

Now if sodium perborate should be adopted by the laundry in place of chlorine bleaching compounds, it could be employed in hot solutions without danger of rapid destruction of cotton materials, and even its use would be a distinct advancement over that of either chloride of lime solutions or electrolytic bleach liquors where these are employed with skill

and judgment. When the effect on woolen and silk goods is to be considered, it must be borne in mind that the solutions prepared from sodium perborate contain a large amount of caustic soda, and unless this is properly neutralized by the addition of sulphuric acid, it will be very destructive to the animal fibers. It is, therefore, a question as to whether the laundry would be any safer on this line of goods by the use of sodium perborate. However, when considered in its general effect, we can see a distinct advantage in the use of sodium perborate for laundries over the present methods. But would not hydrogen peroxide itself be a far better agent for the laundry? for it would figure out cheaper than sodium perborate, and it could be used without fear on both cotton and animal fibers alike, just as it comes into trade without needing any skilled manipulation by the user, as is the case with sodium peroxide and perborate. The only advantage we can see for the sodium perborate is the fact that it can be employed in various scouring mixtures, such as soap, alkali, etc., to be used by the laundry in hot solutions; and whether this is an advantage to an intelligent laundryman or not is a question.

It is in this latter field, however, that sodium perborate is acquiring some trade. In Germany there are quite a number of proprietary mixtures on the market for the use of the laundry, which combine both a scouring and a bleaching effect. We meet with such compounds, for instance, as "Persil," which is a mixture of soap, soda ash, silicate of soda, and a small amount of sodium perborate. "Clarax" is another such compound, consisting of a mixture of borax, sodium phosphate, and sodium perborate. "Ozonit" is another proprietary mixture very similar to "Persil" and consisting of about the same ingredients in a somewhat different proportion. In England there are to be met a number of compounds known under the general title of "Perborin" products. Perborin, itself, is pure sodium perborate; Perborin M is a mixture of the perborate with soap and alkali especially designed to meet the requirements of the laundry trade for a combined scouring and bleaching compound.

During the past year, perborate compounds have appeared on the American market, but as yet the general trade is but little acquainted with them. It is probable, however, that if they are properly presented to the laundry trade as a substitute for the present chlorine bleaching compounds, they would meet with a rather ready acceptance.

BOOK REVIEWS.

Sewage Disposal. BY LEONARD P. KINNICUTT, C. E.-A. WINSLOW and R. WINTROP PRATT. John Wiley & Sons. 409 pages, 113 figures indexed.

This excellent book is a general survey on the sewage disposal problem from the various viewpoints of the chemist, the sanitary biologist and the engineer, with particular reference to the conditions

of American practice. The fundamental principles of chemistry and bacteriology are discussed, as well as their application to engineering practice. The authors have been assisted in preparation by many engineers, as is noted in the preface. The work is divided into thirteen chapters, as follows:

Chapter 1. Composition of Sewage.

Chapter 2. Disposal of Sewage by Dilution.

Chapter 3. Screening and Straining of Sewage.

Chapter 4. Preliminary Treatment of Sewage by Sedimentation.

Chapter 5. Preliminary Treatment of Sewage by Chemical Precipitation.

Chapter 6. Preliminary Treatment of Sewage by the Septic Process.

Chapter 7. Disposal of Sewage Sludge.

Chapter 8. Purification of Sewage by Broad Irrigation and Sewage Farming.

Chapter 9. Purification of Sewage by Intermittent Filtration through Sand.

Chapter 10. Purification of Sewage by Contact Beds.

Chapter 11. Purification of Sewage on Trickling and Percolating Beds.

Chapter 12. Disinfection of Sewage and Sewage Effluents.

Chapter 13. Analysis of Sewage and Sewage Effluents.

The reviewer knows of no so complete work in the English language. The subjects in the different chapters are treated scientifically, and intimate personal connection with the facts is evidenced throughout the whole work. Nearly every part of the sewage disposal field has been covered by this book and in a manner which will be most satisfactory to sanitary engineers and advanced students of the art. The omissions are few and comparatively unimportant, for example under self-purification of streams it would have been well to include the work of Spitta and others on the effect of algae as an agent of purification; also the important part which insects and the higher animals play in the removal of organic matter contributed to streams by sewage and sewage effluent, might have been mentioned. The illustrations in the book are especially valuable and there is some statistical matter which has appeared in book form for the first time. Even so recent an invention as the Imhoff or Emscher tank has been commented upon. This fact is an evidence of the thoroughly up-to-date character of the subject matter of this most valuable treatise.

R. S. WESTON.

Le Celluloid.—Fabrication, Applications, Substitutes. BY MASELON, ROBERTS and CILLARD. 520 pages, illustrated. Paris: A. D. Cillard. 1910. 20 francs.

The book is divided into three parts. The first part is devoted to the preparation of celluloid from the raw materials. In it are described various processes of nitration; converting of the nitrocellulose; plans, organization and cost of plant; laboratory control; dangers in manufacturing and precautions to be taken.

The second part is devoted to the working of celluloid. After a preliminary chapter on general principles, the making of combs is described with details as to plant machinery and output; then follow descriptions of the process of molding and other operations required in making balls, boxes, handles and numerous other articles; the artificial linen industry; the art of stamping and pressing; covering of articles with celluloid; decoration; solutions; films for use in photography; and special uses of celluloid.

The third part treats of non-inflammable celluloid, camphor substitutes, celluloid substitutes and cellulose acetates.

In a work as ambitious as the above it is not surprising that there should be some mistakes, errors, and omissions. In the first chapter, the invention of celluloid which belongs to Daniel Spill, of Hackney, England, is credited to Hyatt. The chapter on nitrations gives many impossible processes, notably one by Mowbray of North Adams. A large part of the chapters on bleaching and dehydration of the nitro-cellulose are devoted to obsolete and impracticable methods. The laboratory control of the nitration and other process while giving a good outline of the work required is faulty in its methods and calculations. Finally it might be added, in concluding this unfavorable criticism, that the book is somewhat one-sided in giving undue space to Part II on the working of celluloid which might better be devoted to its manufacture.

The authors have undoubtedly filled a great void in industrial chemical literature by their contribution. The best works on industrial chemistry hardly describe the manufacture of celluloid at all and the special works on the subject have hitherto contained little or nothing of value. The outline of manufacturing operations given should recommend itself to students and the presentation of the precautions necessary in handling celluloid is most valuable to those engaged in this industry, many of whom are quite ignorant on the subject. The descriptions on the many and increasing uses of celluloid together with the size of shops, machines, apparatus, power and labor required in fashioning it should do much to further the use of this valuable product.

M. JOYCE.

Municipal Chemistry. A series of thirty lectures by experts on The Application of the Principles of Chemistry to the City, delivered at the College of the City of New York, 1910, edited by CHARLES BASKERVILLE, PH.D., F.C.S., Professor of Chemistry and Director of the Laboratory, College of the City of New York. McGraw-Hill Book Company, 239 West 39th street, New York; 6 Bouverie Street, London, E. C. Price, \$5.00 net.

"A careful study of municipal affairs shows that the greatest material need of our American cities to-day is the chemist. It is unfortunately true that the position of the chemist in the municipal body politic is uncertain, if indeed it exists. This is due in a measure to the conception of the rôle of a chemist by the people, who look upon him as an analyst and not as an important social factor."

"The successful manufacturer spends money willingly to improve the efficiency of his machinery. It is positive and not negative economy that counts most. Superior sanitary conditions affect human efficiency in the same way, and those who are benefited are the better able to pay for it."

These extracts from the preface of the volume which Professor Baskerville has sent into the world outline pretty well the object and aims of this work. After an introductory chapter on the sanitation in the city by the author himself, follow no less than twenty-nine chapters under different authorship, on the most varied subjects relating to the chemistry of sanitation, hygiene, food, clothing, road construction, street cleaning, etc.

The subjects are handled by experts and are, in substance, the reproduction of lectures delivered at the College of the City of New York by these specialists.

Professor Baskerville has utilized to the best advantage his many friendly relations, and succeeded in arousing enough enthusiasm to get so many distinguished men to lecture at the College of the City of New York. He thus was able to present us a volume which ought to be in the hands of everybody who is interested in the sanitary or other chemical engineering problems, which confront large and small cities. His book should specially be read and consulted by everybody who is directly or indirectly connected with the Board of Health, as well as by the city engineers.

The immensity of the subject and the limitations of this book of 503 pages have compelled the different collaborators to restrict their subject to some suggestive generalizations. Some of the lecturers have furnished full references to the literature of their subject. Others have sadly omitted this important information. To the reader who looks for more knowledge on the subject, it would have been desirable if the book had been supplemented by a very complete list of literature references. This is an unfortunate and very serious omission in some of the chapters, which might be corrected in a future edition.

On the other hand, the whole subject is treated in such an accessible style that even those who know nothing about chemistry or biology can easily read the book, and will find it a very fruitful source of interesting information.

L. H. BAEKELAND.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER.

Chemists interested in flour will find an excellent expression of views (both pro and con) on the Alsop process of bleaching flour by NO₂ in "Notice of Judgment" No. 722, published by the United States Agricultural Department. It contains the expert testimony of a large number of witnesses for both sides of this famous case. The pamphlet can be obtained free of charge from the Division of Publications, Washington, D. C.

The recently formed Bureau of Mines, an off-shoot of the U. S. Geological Survey, is making a very creditable showing in connection with its bulletins, and before long its publications will be quite as much in demand as other Government scientific publications. The Bureau does not maintain a regular mailing list, but any one interested can obtain its list of publications which appear periodically. So far, the Bureau's publications have been almost entirely confined to information about fuel, as can be seen by the appended list of bulletins:

Bulletin 1. The Volatile Matter of Coal. 2. North Dakota Lignite as a Fuel for Power Plant Boilers. 3. The Coke Industry of the United States as Related to the Foundry. 4. Features of Producer—Gas Power—Plant Development in Europe. 5. Washing and Coking Tests of Coke. 9. Recent Development of Producer—Gas Power—Plants in the United States. 11. The Purchase of Coal by the Government under Specifications.

Circular 1. Permissible Explosives. 2. Permissible Explosives.

At the 82nd annual meeting of the German Natural Scientists and Physicians, Professor J. Zenneck delivered an address on the "Utilization of the Nitrogen of the Air by means of the Flaming Arc." This is a description of the plant and process as carried out at Notodden, Norway. The pamphlet¹ is written in non-technical language, and contains many excellent illustrations.

Recent publications of interest to chemists: Curie, Mme. P.: *Traité de Radioactivité*; Paris, 1910, Fr. 30. Escales, Richard: *Chloratsprengstoffe*; Leipzig, 1910, M. 8. Groth, P.: *Chemische Krystallographie*; Leipzig, 1910, M. 30. Sedgwick, N. V.: *The Organic Chemistry of Nitrogen*; Oxford, 1910, 14Sh. Ehrlich and Hata: *Die experimentelle Chemotherapie der Spirillosen*; Berlin, 1910. Nathanson, A.: *Der Stoffwechsel der Pflanzen*; Leipzig, 1910, M. 12. Contributions to Economic Geology, 1908, Part 11. By Marius R. Campbell. Bull. 381, U. S. Geological Survey, Washington.

IRON AND STEEL, including Allied Industries and Sciences. By Hugh P. Tiemann, with an introduction by Henry Marion Howe. \$3. McGraw-Hill Book Co., New York.

"CANE SUGAR," discussing the agriculture and manufacture of cane sugar and the analysis of sugar house products. 592 pages, fully illustrated and indexed. By Noel Deerr, Sugar Technologist at the Experiment Station of the Hawaiian Sugar Planters' Association. Published by Norman Rodger, Manchester.

DIVISION OF AGRICULTURAL AND FOOD CHEMISTS OF THE AMERICAN CHEMICAL SOCIETY.

MINNEAPOLIS, DEC. 28-31, 1910.

The first session of the section was held in the Chemistry building, University of Minnesota, on Friday morning, Dec.

¹ "Die Verwertung des Luftstickstoffs mit Hilfe des electrischen Flammenbogens," von Professor Dr. J. Zenneck. Leipzig, 1911. S. Hirzel. M. 1.60.

30th. The meeting was called to order by Mr. H. E. Barnard, Chairman of the Section.

The following papers were presented:

H. E. Barnard, Some Poisons in Foods.

Fred W. Morse, The Soluble Carbohydrates in Asparagus Roots.

E. H. S. Bailey, Composition of the Ash of Pickles.

M. E. Jaffa, The Examination of Some California Alfalfa.

Herbert M. Shilstone, Sugar By-Products.

Floyd M. Robinson, Coffee and Coffee Substitute Extracts.

A. N. Cook, The Relative Toxicity of Substances Added to and Occurring Naturally in Foods.

E. H. Harding and Miss Lilian Nye, Quantitative Method for Determining Non-Volatile Oil in Cereals.

Payne B. Parsons and Geo. A. Soper, Dissolved Oxygen as an Index in Sewage Pollution.

Payne B. Parsons and Geo. A. Soper, The Determination of Dissolved Oxygen in Water.

Julius Hortvet, The Composition of Some So-called Malt-Tonics.

Edwin DeBarr, The Examination of Beverages for Caffeine and Other Alkaloids.

E. B. Holland, Purification of Insoluble Fatty Acids.

Chas. P. Fox, Excrements of Guayule Fed Goats.

G. B. Frankforter and Ben Hur Kepner, Chemical Study of Wheat, Part 2.

A. W. Blair and S. E. Collison, Preliminary Report on the Loss of Lime in Some Drainage Water.

After the papers had been presented and the discussions closed the following business was transacted.

The following resolution was presented to the division:

Recognizing the irreparable loss incurred by the agricultural and food chemists of America through the death of Albert E. Leach, long analyst of the Massachusetts State Board of Health, late chief of the Denver Laboratory of the U. S. Bureau of Chemistry, skilful analyst and valuable contributor to the success of analytical chemistry, we, the members of the division of agricultural and food chemistry of Section C of the A. A. C. S., do hereby express our deep sorrow at the passing of our friend and fellow and extend to his bereaved family this token of our sympathy.

It was moved, seconded and voted that the resolution be adopted. The secretary of the division was instructed to send a copy of the same to Mrs. Leach.

The matter of financing the division was discussed. The matter was left with the executive committee with power to act.

The chairman and secretary were instructed to revise the list of members of the section and secure the enrollment of agricultural and food chemists not now on the roll.

The following officers were elected for the ensuing year:

Chairman, H. E. Barnard,

Vice-Chairman, A. L. Winton,

Secretary and Treasurer, B. E. Curry.

Executive Committee:

F. W. Robison,

H. W. Wiley,

J. P. Street,

G. F. Mason.

B. E. Curry, *Secretary*.

NOTES AND ABSTRACTS FROM CONSULAR REPORTS.

Consul H. P. Coffin reports in the Province of Santa Fe, Argentine, 2,951 industrial establishments, 2,456 of which are owned by foreigners. The annual output of the sugar mills is

estimated at thirteen million dollars U. S. gold, and the flour mills at eight million dollars.

Consul A. A. Winslow, of Valparaiso, reports that much attention is being given to the production of wood pulp in Chili, and it is understood that the Government is ready to encourage the development of the industry, which seems likely to be of considerable commercial importance as there is an abundance of the raw material suitable for production of wood pulp.

Consul Augustus Ingram, of Bradford, Eng., reports that the City Council in Bradford has authorized the expenditure of \$155,000 for the installation of vertical retorts in the city gas works. The vertical retorts have been widely adopted in Germany during the last few years, but Bradford is one of the first cities in England to adopt the system.

The Stavanger Electro-Staalverk Co. is being organized, capital \$120,000, to establish a plant for making high-grade steel electrically, using a process similar to that now used in Dommarfvet, Sweden, and elsewhere.

The new company plans to take over the plant of the Stavanger Skibs-Ophugnings Co., and continue purchasing and breaking up old steel and iron vessels. The company will also secure raw materials from other sources and instal modern machinery for making fine quality steel. The new plant is being located at the near-by village of Jorpeland, where electric power has been secured at \$6.70 per horse-power per year for the first 1,500 horse-power and \$5.35 for 1,000 more horse-power delivered at the power shaft; 10,000 horse-power will be available when needed.

The full yearly capacity of the plant will be 1,400 tons high-grade steel billets, 600 tons steel castings, 300 tons hammered steel, and 700 tons refuse for smelting.

700,000 rubber trees are growing on the island of Trinidad, and the number will be greatly increased during the next few years.

The importation of foreign sugar into India for the first ten months of 1910 amounted to 6,182,570 pounds compared with 4,540,292 pounds for the same period in 1909.

Consul C. A. Miller reports a shipment of 30,000 barrels of asphalt from Tampiko to Canada.

In the annual financial survey published by the Toronto (Canada) *Globe*, Mr. Alexander Gray estimates the silver shipped by the mines in the cobalt district of Ontario in 1910 at 28,500,000 ounces, valued at \$14,500,000. In 1909 the output was 25,897,825 ounces, worth \$12,461,576, and in 1908 the production amounted to 19,437,875 ounces, valued at \$9,133,378.

The quantity of asphalt taken from Pitch Lake, which covers an area of 100 acres, during 1910 exceeded that of any previous year. At the present rate of operation the surface level is lowered about 6 inches a year. The depth of the deposit of asphalt over the center of the lake is unknown, as it cannot be sounded by rods, but the supply is supposed to equal the demand for many years; possibly it is inexhaustible.

The cotton spindles of the world number roundly 134,000,000, of which about 54,000,000 are in the United Kingdom, and a large proportion of these are in Lancastershire and sections immediately adjacent. The magnitude of England's cotton industry is amazing and its importance to the maintenance of her commercial supremacy and to the great prosperity and welfare of the people of the entire Kingdom can not be overesti-

mated. The annual export of manufactures of cotton, valued at approximately \$500,000,000, constitute nearly one-fourth of the entire \$2,280,000,000 exports of the Kingdom. In addition to the exports the mills supply for home consumption cloths to the value of approximately \$100,000,000 annually.

WAGES OF UNSKILLED LABOR IN GERMANY.

According to a report published by the *Imperial Official Journal*, the average daily wages paid unskilled adult male laborers during the year 1910 in the following cities, each having a present population of 200,000 or more, as compared with the average wages paid during the year 1893, were as follows:

Cities.	1893.	1910.
Munich.....	\$0.547	\$ 0.880
Berlin.....	0.643	0.857
Charlottenburg.....	0.595	0.857
Rixdorf.....	0.571	0.857
Leipzig.....	0.476	0.833
Düsseldorf.....	0.571	0.833
Stuttgart.....	0.595	0.833
Hamburg.....	0.619	0.809
Frankfort.....	0.596	0.809
Nurnberg.....	0.524	0.809
Essen.....	0.571	0.809
Dresden.....	0.595	0.785
Dortmund.....	0.476	0.785
Cologne.....	0.595	0.774
Duisburg.....	0.571	0.774
Bremen.....	0.714	0.762
Kiel.....	0.643	0.762
Breslau.....	0.476	0.714
Hanover.....	0.571	0.714
Magdeburg.....	0.476	0.714
Königsberg.....	0.595	0.655
Chemnitz.....	0.524	0.595
Stettin.....	0.536	0.595
Average.....	0.596	0.774

WORLD'S TIN SUPPLY.

(From advance chapters of Geological Survey publications.)

Recovery of tin from tin scrap, used tin cans, old tin pipe, worn driving-box linings, drosses, old solder, bronze, sweepings, etc., in the United States is increasing. From these materials the recovery of tin is commonplace and expected except from used tin cans; in them the loss of tin is enormous. The tin recovered during 1909 as tin amounted to 2,423 short tons; in the form of alloys, such as solder, babbitt metal, bronze, etc., 3,092 tons; a total of 5,515 tons, equal to more than one-ninth of the tin imported into the United States and worth \$3,281,425. Besides the money value involved, the world's tin resources were increased by so much—a very real conservation.

The world's supply of tin for the years 1907, 1908, and 1909, as shown by total shipments and sales from various countries, was approximately as follows:

	1907. Tons.	1908. Tons.	1909. Tons.
Total shipments:			
Straits Settlements.....	58,800	67,760	65,459
Austria.....	7,112	6,552	5,992
Bolivia.....	17,136	19,040	23,523
South Africa.....	...	1,904	916
China.....	224
Bank sales in Holland.....	12,197	12,880	12,992
Billiton sales in Java.....	2,408	2,465	2,465
Production in Cornwall.....	5,488	6,048	5,802
Total.....	103,365	116,649	117,149

INCREASING GUAYULE RUBBER SHIPMENTS FROM MEXICO.

Consul Wilbert L. Bonney reports that the declared exports of Mexican products *via* San Luis Potosi to the United States amounted to \$4,395,384 in 1910, an increase of 29 per cent.

over 1909. The largest increase was in guayule rubber, being \$1,224,222 for 1910, against \$294,239 for 1909. This article appeared in the exports of that district for the first time in 1901, but did not rise to importance until 1908.

SOME VALUABLE MINERALS IN UNITED STATES.

(From advance chapters of Geological Survey publications.)

The estimated production of antimony in the United States for 1909 was: Contained in antimonial lead of domestic origin, \$252,252; contained in antimonial lead of foreign origin, \$115,908; recovered from old alloys, etc., \$242,736. Imports of antimony metal and regulus during the year, aggregating 9,557,956 pounds, were larger than in 1908 and practically equal to the imports for 1907; but the value, \$620,117, was less than that in 1908 and not half the value in 1907. The price of antimony was fairly steady during 1909.

The total quantity of arsenic recovered as a by-product in smelting in 1909 was 2,428,313 pounds, valued at \$52,946. The average market price was 2.97 cents per pound. There were imported during the year from Canada, Europe, and Mexico white arsenic, metallic arsenic, and arsenic sulphides valued at \$303,728, and Paris green and London purple worth \$20,370. A large part of the white arsenic is made into Paris green for use as an insecticide.

Bolivia is the principal bismuth-producing country, and from it, during 1909, bismuth ore valued at \$188,574 was exported. Smaller quantities were produced in Queensland, New South Wales, and Tasmania. Other countries that are either actual or possible producers are Bohemia, Mexico, Norway, Peru, Portugal, Saxony, and Spain. The only production of bismuth in the United States during 1909 reported to the Geological Survey was by a firm in Indiana which made it as a by-product of an electrolytic lead refinery. The 1909 imports of metallic bismuth were valued at \$286,516, compared with \$257,397 in 1908. The price of bismuth and its compounds is closely governed by foreign firms, and was quoted during 1909 at \$1.70-1.80 per pound.

Selenium is known to have been made during 1909 at only one place in the United States, where a comparatively small quantity was saved. It was sold at an average price of \$3.43 per pound. [Selenium is a poor conductor of electricity, but its resistance diminishes on exposure to light, and this property has been made use of in wireless telephony.—B. M.]

PRIZE FOR DISCOVERING COCONUT DISEASE.

President Gomez approved a bill on December 13th, offering a prize of \$30,000 to the individual, native or foreign, who discovers the origin of the disease which attacks and kills the coconut trees in the island of Cuba, and the means necessary for its cure and prevention. The prize is to be paid when it is shown to the satisfaction of the Government that the discovery has actually been made and that the cure is efficacious. The disease in question is a kind of "bud rot," which is said to have made its appearance in Cuba prior to 1871, and although repeated efforts have been made to put an end to its ravages, no effective means has as yet been found except the destruction of the plant affected.

INCREASED GERMAN PRODUCTION OF POTASH.

It is announced that the Bundesrat has considerably increased the quantity of potash which can be produced by German potash works during the period from May 1 to December 31, 1911, amounts in metric tons of 2,204.6 pounds pure potash (K_2O) which can be sold without being subjected to the special tax are now fixed as follows, with comparison of amounts as determined in June, 1910:

Classification.	For home consumption.		For exportation.	
	Old allowance. Tons.	New allowance. Tons.	Old allowance. Tons.	New allowance. Tons.
Carnallite with 9-12 per cent. K_2O	3,000	3,580	110	100
Crude salts with 12-15 per cent. K_2O	126,820	140,000	19,600	20,000
Salts for fertilizer with 20-22 per cent. K_2O	880	1,000	11,000	11,800
Salts for fertilizer with 30-32 per cent. K_2O	320	1,270	9,020	9,020
Salts for fertilizers with 40-42 per cent. K_2O including potash fertilizer with 38 per cent. K_2O .	37,540	41,740	14,750	17,950
Chlorate of potash.....	35,250	40,750	55,760	104,360
Sulphate of potash with over 42 per cent. K_2O	1,020	1,020	3,200	28,900
Potassium magnesium sulphate...	100	100	4,640	4,640
Total.....	204,380	219,780	198,140	282,590

It will be seen that the recent action of the Bundesrat has increased the production, free of special taxation, for the period from May 1 to December 31, by about 100,000 metric tons.

NEW COMPANIES IN CHINA.

Consul General Leo Bergholz of Canton reports that the Kwang-si Industrial Company, with a head office at the Provincial Capital (Kwei-lin) and branches in other parts of the Province, has been organized to promote the agricultural and industrial development of Kwang-si, and has already located and contemplates developing more than 200 coal, iron, silver, gold, and copper mines. A large share of the initial capital has been subscribed by Chinese in the United States and, failing the subscription of the balance in China, it is probable that a foreign loan will be raised.

Another company, capitalized at over \$1,000,000 gold, is successfully working the silver mines in Kwei-hsien, in the same Province, and a third company, with a capital of \$80,000 gold, is mining tin at Ho-Yuen.

It is reported that the governor of Wang-hsi has entered into negotiations with the Banque de l'Indo Chine, in Peking, for an unsecured loan of \$4,380,000 to be employed in the encouragement of various industries in his Province.

NEW METHOD OF METAL COATING.

Consul General Frank H. Mason, Paris, reports that the principle involved in the new method of coating various substances with metals, which process is the invention of a Swiss engineer and was recently presented before the Academy of Sciences at Paris by a member of the institute, consists in reducing molten tin, zinc, copper, lead, aluminum, or other metal or alloy to a state of pulverization by the pressure of an inert gas—nitrogen or hydrogen—and in that state driving it against the surface to be covered from a flexible tube with a tip like that of a large vaporizer for liquids.

This is said to produce a metallic coating similar to the deposit of copper on an electrotype plate by the galvanic process, the difference being that by the new process, the method of coating is mechanical and immediate, not dependent upon chemical action, and therefore applicable to a wide range of substances under any conditions which permit the apparatus to be used. For ordinary purposes the metalizing plant is stationary, but for metal coating large surfaces in or out of doors a portable apparatus has been devised which is said to give satisfactory results.

RUBBER INVESTMENT IN NETHERLANDS, INDIA.

Consul B. S. Rairden (Batavia, Java) reports that \$78,935,200 capital was invested in rubber cultivation in the Nether-

lands, India up to the end of June, 1910. The investments up to 1909 had been \$14,608,400, while the rubber investments in 1909 were \$15,926,000.

PREVENTION OF WASTE AND RIVER POLLUTION.

In a concentrated wool-manufacturing district such as the West Riding of Yorkshire, devoted to an industry requiring the use of immense quantities of water every day, the task of keeping the small streams near the inland English cities in a healthy condition is not an easy one. The Colne and Holme Rivers at Huddersfield are black with the refuse contained in the waste waters from the milling, scouring, and dyeing processes.

As a result of the official activities of the West Riding Rivers Board, and also from a desire for more economical production, manufacturers are using various methods to cope with this problem, one of which is believed to be highly successful. This method deals with the main cause of stream pollution—namely, wool and piece scouring—and seeks to prevent the loss of large quantities of the oil, grease, fiber, soap, and scouring materials heretofore usually carried off by the water as waste products.

NOTES.

"Atherium" is a new aluminum alloy being offered by Pritt, Bowley and Company, 46 Fenchurch Street, London, E. C., which is expected to be of considerable value in the arts. It has the following properties:

Specific gravity: 2.4–2.57, according to the mixture.

Tensile: 18.66 tons to the square inch.

Yield point: 33,712 pounds to the square inch.

This alloy is said to form sound castings and work well in the rolling and turning; it can also be soldered, forged and welded, and does not tarnish or corrode. It stands the action of sea water.

The increased demand for tungsten lamps has made it necessary for the Westinghouse Lamp Company to reoccupy the plant on West 23rd Street, New York, which they abandoned in 1908 for their new works in Bloomfield, N. J.

The old factory has been equipped with newly developed machinery of American design, for the manufacture of 25, 40, and 60 watt tungsten lamps. The capacity will be 10,000 lamps per day.

A neon tube light, similar to the Moore light, has been briefly described before the French Physical Society, by M. Georges Claude. The substitution of the neon for carbon dioxide or nitrogen in the Moore tube is said to give a light very rich in red rays of a remarkably warm, golden yellow hue.

The vertical retorts installed at Providence by the Providence Gas Company are attracting considerable attention among gas engineers, and the New England Association of Gas Engineers visited Providence to inspect this installation during their annual convention in Boston in February.

Mr. Andrew Carnegie had added \$10,000,000 to the endowment fund of the Carnegie Institution of Washington. The institution was established in 1902 with a gift of \$10,000,000, and Mr. Carnegie recently added \$2,000,000. These gifts consist of preferred bonds of the U. S. Steel Corporation bearing 5 per cent. interest and their market value is considerably above their par value. Mr. Carnegie's gifts to public purposes now amount to about \$200,000,000.

The next Faraday lecture of the Chemical Society of London

is to be given on June 14th by Professor Theodore W. Richards, of Harvard University, in Faraday's lecture room at the Royal Institution.

Additional grants have been made to Professor T. W. Richards and to Professor G. P. Baxter, of Harvard University, of \$2,500 and \$1,000, respectively, as research associates of the Carnegie Institution of Washington.

On January 20th, Professor Arthur Michael lectured before the members and research students at the department of chemistry at Clark University on his recent observations in connection with reversible organic chemistry. A result of the greatest importance is Professor Michael's discovery of an apparently new factor influencing the velocity of organic reactions.

The United States Civil Service Commission announces an examination on March 29, 1911, to secure eligibles from which to fill the position of editorial assistant in the Bureau of Mines, Department of the Interior, at a salary of from \$1,200–1,500 per annum, according to qualifications. The examination will consist of the subjects given below, weighted as indicated:

1. Editing.....	30
2. Proof reading.....	20
3. Thesis.....	30
4. Education and experience.....	20
	100

Applicants should apply to the United States Civil Service Commission, Washington, D. C., for full information and registration blanks.

Slate quarry waste has been employed as a filler for fertilizer, for making paint for flagging and for mending roads, but none of these uses are a source of income. In Norway slate waste has been mixed with casein and hardened, the resulting product being very much like freshly quarried slate in appearance and properties.

Mr. Carnegie's latest gift of \$3,800,000 to the Technical Institute in Pittsburgh is to be used approximately as follows: \$2,300,000 for new buildings, \$100,000 for additional equipment and \$25,000 on grounds.

The Bureau of Mines has just issued "Miners' Circular No. 2" by Clarence Hall, on "Permissible Explosives."

This circular states the conditions under which explosives are accepted for testing, the tests the explosives now have to pass, the names of the explosives that have passed the tests, and some of the dangers that should be avoided in storing and using explosives. The United States Geological Survey, which formerly had charge of the station at Pittsburgh, Pa., has published in three circulars the names of the explosives that passed similar tests prior to May 16, 1910. All of those explosives, and all permissible explosives subsequent to May 16, 1910, and prior to January 1, 1911, except such as have been withdrawn by the makers or have not satisfied later tests, are named in this circular.

Twelve street cars have been put into service in Zurich in which all of the metallic portions of the body are made of aluminum. In addition to the advantage of lightness, it is found that when the metal is cleaned with the sand blast it is effectively protected by paint without the use of varnishes.

An explosion near the station of the Central Railroad of New Jersey in Jersey City occurred on Wednesday, February 1st, in which twenty-five or more people were killed, and the property

damage is estimated at two hundred thousand dollars. The dynamite was being unloaded from a freight car and transferred to a lighter. Every member of the crew of the lighter and another vessel alongside was killed. A number of freight cars were wrecked, and considerable damage was done to the passenger station and ferry boats lying at the slip. The force of the explosion was felt forty miles away. No satisfactory explanation has been given as the cause of the disaster.

The New York Central Lines have ordered for 1911 delivery 41,500 tons of titanium steel rails. The specifications call for the use of 1 per cent. of a 10 per cent. alloy (or equivalent) of titanium.

The production of spelter in the United States for the year 1910 was 246,680 tons compared with 236,660 for 1909. The world's production for 1910 is estimated at 802,000 tons.

The U. S. Geological Survey reports the production of monozite in this country during 1909 to be 541,931 pounds, valued at \$65,032. There were also 69,998 pounds of monozite and thorite imported valued at \$8,324, and 17,549 pounds of thorium oxide and salts other than nitrate valued at \$19,596. There was imported of thorium nitrate, the mantle chemical, 127,833 pounds, valued at \$236,057.

The production of coal tar in Great Britain during the last year is estimated at from 800,000-900,000 tons, of which 600,000 is distilled.

Estimated distribution of the product: Coal tar manufactures, 2 per cent.; water, 3 per cent.; light naphtha, 3 per cent.; middle oil, 8 per cent.; creosote oil, 10 per cent.; anthracene oil, 10 per cent.; pitch, 61 per cent.; loss, 3 per cent.

Official estimates of the Interior Department, Canada, place the available water power of the Dominion of Canada at 25 million horse-power—equivalent to over 562 million tons of coal per annum. The Province of Quebec is estimated to have 17 million horse-power, of which only 50 million are now developed. Ontario is estimated at 3 million horse-power, of which 330 thousand are now developed.

The Niagara Falls Power Company and the Canadian Niagara Power Company announced a pension system for their employees, effective January 1, 1911. Men 50 years of age, who have been in the service of the Companies for 15 years, may be retired on a pension of not less than twenty dollars per month, or more than one hundred, according to their earning power.

In a study of the firefly, by H. E. Ives (*Physical Review*, December) the author concludes: "The results of the present investigation may be said to render still more probable the belief that the firefly produces only visible radiation of high efficiency. There is no evidence that the light is due to anything other than a true production of light by some biochemical process."

The production of crude petroleum in the United States in 1910, as reported by Dr. David T. Day, of the United States Geological Survey, was between 200 million and 208 million barrels. Dr. Day makes the following distribution of the production:

	Barrels.
Illinois.....	32,000,000
Appalachian and Lima-Indiana Fields.....	32,000,000
Gulf and Caddo Fields.....	14,000,000
Mid-Continent and Rocky Mountain Fields.....	53,000,000
California.....	73,000,000
	204,000,000

The United States Geological Survey reports the discovery of phosphate rock in Montana, in what is believed to be valuable commercial quantities. The deposits are found not far from Butte, and as they are situated on public lands, these have been withdrawn from entry by the President, and placed in the same category as other public lands awaiting legislation by Congress to provide for their control and disposition. Now that the lands have been withdrawn from entry, it is proposed to make a detailed geological investigation of these deposits and report upon their scope.

The development of the metal filament lamp industry in England is indicated by an article in the *Electrician* illustrating and describing the new Imperial Lamp Works at Brimsdown. This factory is built for the exclusive manufacture of tungsten lamps under the patents of Dr. Küzel, which cover the use of the tungsten in the colloidal form. The present output of the factory is two and half million lamps per year, with an additional capacity to bring the output up to five million lamps.

The assignment of the American patents for a method of making phosphorus matches without the use of white phosphorus to a committee of trustees of consisting of Professor Seligman, Commissioner Neale, and Mr. Ralston, as announced in the February issue of *THIS JOURNAL*, was found to be objectionable to certain members of Congress. As this course was considered to endanger the bills before Congress preventing the use of white phosphorus, the Diamond Match Company thereupon voluntarily renounced ownership of the patents and dedicated them to the free use of the people of the United States.

The Census Bureau reports that tan bark and tanning extracts were consumed in the United States during the calendar year 1909 to the value of \$21,904,927, as against \$21,361,719 in 1908 and \$21,205,547 in 1907.

According to reports received by the United States Geological Survey from coal mine operators and others familiar with the industry, the production of coal in the United States during 1910 was between 475,000,000 and 485,000,000 short tons compared with 459,715,704 short tons in 1909 and 480,363,424 tons in 1907.

Of the total production in 1910 the anthracite mines of Pennsylvania contributed nearly 83,000,000 short tons and the bituminous mines between 390,000,000 and 400,000,000 tons.

C. L. de Mural, recently appointed professor of electrical engineering at the University of Michigan, becomes editor of the *Railway Electrical Engineer*. This journal is the official organ of the Association of Railway Electrical Engineers.

Mr. C. E. Bradley has resigned as chemist of the Agricultural Experiment Station at Corvallis, Oregon, to accept the position of research chemist with the Rubber Regenerating Company, of Mishawaka, Indiana.

The Harvard University Catalogue shows this year a total enrolment of 4,123 students in the university exclusive of the summer schools, Radcliffe College, and the university extension courses. The total number of students is 77 more than it was at the corresponding period last year.

The third semi-annual meeting of the American Institute of Chemical Engineers will be held at Chicago, Ill., June 21-4. Arrangements will be made to visit a number of the large technical plants in the vicinity. The committees on chemical engineering education and standardization of boiler tests will

have important reports to present. The program of papers will be announced later.

The new \$300,000 engineering building, and the new \$150,000 power plant of the University of Cincinnati are rapidly nearing completion. The engineering building is of reinforced concrete and stone, four stories in height, built to accommodate five hundred students.

Among the main features of the building will be a large laboratory 200 × 40 feet in size. This laboratory will be surrounded by balconies, which will give a much larger floor space than is indicated by the dimensions of the room itself. In addition to this there will be a large general club room for the students taking the regular engineering courses. There will also be a large consulting library, solely for the use of the College of Engineering.

The building will be fire-proof throughout and of the best possible construction. One marked feature of the building will be the absence of a great mass of heavy machinery which is usually found in engineering colleges. The students will have the use of the latest and most improved machinery in all of the different manufacturing industries having plants in the city of Cincinnati. This condition has permitted the use of space which would have otherwise been occupied by machinery for extensive scientific and research laboratories.

Production of pig iron in the United States was larger in 1910 than in any other year, according to the official figures prepared by James M. Swank, secretary of the American Iron and Steel Association. Returns published this week showed that the output by leading States had compared as follows, in tons:

	1910.	1909.	1908.
New York.....	1,938,407	1,733,675	1,019,495
Pennsylvania.....	11,272,920	10,918,824	6,987,191
Virginia.....	444,976	391,134	320,458
Alabama.....	1,939,147	1,763,617	1,397,014
Ohio.....	5,751,067	5,551,545	2,861,355
Illinois.....	2,675,646	2,467,156	1,691,944
Ind. & Mich.....	1,250,103	964,289	348,096
Total.....	27,298,545	25,795,471	15,936,018

The production of pig iron in Pennsylvania in 1910 was 41.3 per cent. of the total produced by the whole country.

Dr. Arthur H. Elliott, consulting engineer-chemist for the Consolidated Gas Company of New York, has given a very interesting series of lectures before the classes of mines, engineering and chemistry in Columbia University. These lectures were given at the conclusion of the instruction on the chemistry of gas manufacture, and were particularly designed to show the problems involved in gas-making and distribution on a large scale, with especial reference to recent improvements in the art. The scope of the lectures is indicated by the following headings: "Recent Improvements in Gas Manufacture;" "Gas Purification;" "Recent Improvements in Gas Purification;" "Use and Abuse of Gas;" "Valuation of Gas."

The Bureau of Standards is ready to supply the following new analyzed samples: No. 29, titaniferous magnetite ore, from New Jersey. No. 11a, basic open-hearth steel with 0.2 per cent. carbon. No. 12a, basic open-hearth steel with 0.4 per cent. carbon. The steels replace the original samples which are exhausted. Renewal samples of Bessemer steels with 0.1 per cent. and 0.2 per cent. carbon are in process of analysis, also a nickel and a chrome-vanadium steel.

Factory fires and fire hazards are discussed at considerable length in the February 7th issue of the *Survey*. The recent casualty in Newark, in which 25 people lost their lives, is de-

scribed in detail by Mr. P. J. McKenon. Drawings and photographs are produced to show how the accident occurred, and what means might have been taken to prevent it. A number of pictures are produced to show the carelessness of factory managers in providing proper safety means for their employees.

"Warding Off Factory Fire Panics and Its Loss of Life," by Mr. H. F. P. Porter, is the title of the second article in the same issue. Fire drills, fire alarm system systems, and fire-fighting organizations are described in considerable detail; reference is made in this article to the simple means at hand for preventing serious disasters.

The time for the opening of the new Chemists' Building in New York is rapidly drawing near, and the program for the opening exercises is practically completed. The various chemical organizations in New York and vicinity will take part in dedicating the new home of the Chemists' Club. Since the project of the Chemists' Building was first started, about two years ago, the Club has doubled its membership.

Dr. Fritz Zerban, formerly assistant to Professor Charles Baskerville, and of late Director of the Chemical Department of the Argentine Agricultural Experiment Station, was recently in New York on his way to Porto Rico, where he will have a similar position with the Experiment Station there. Dr. Zerban is specializing in sugar chemistry.

President Ira Remsen, of Johns Hopkins University, was recently elected an honorary member of the Chemical Society.

RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, 908 G St., Washington, D. C.

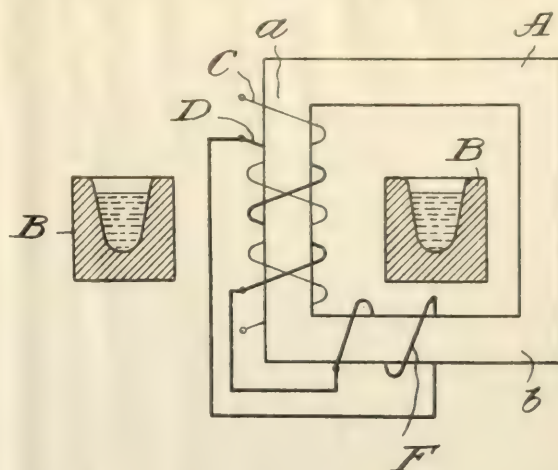
980,813. Process of Liquefying Air and Separating Out Oxygen.

This invention is a process of liquefying air and separating gases with a partial recovery of the energy consumed by the compression. It differs from older processes very materially in its respect, that, for the purpose of reducing the pressure behind the expansion chamber in the exhaust port of the expansion engines (piston engines, Laval or Parsons' turbines or the like) the expanded gases are not sucked off by the compressor, but by a special device (suction pump or the like), thus producing a partial vacuum in order not to let cold expanded gases reenter the compressor, but to drive them out into the open air after using them as far as possible as cooling medium for the process itself, in order to obtain in this way a mixture of fluids rich in oxygen. This is greatly facilitated by not sending back the expanded gases into the circuit, but by driving them out after a more perfect exchange of heat has taken place. The new technical effects gained in this way over other processes for liquefying air in which the expanded gases, after having done their work, are led off under atmospheric pressure, consist in the first place, in consequence of the greater lowering of the pressure, the falling of the temperature is correspondingly greater, that secondly the engine is not stopped as is the case with Siemens and other similar devices by a great lowering of the temperature, and thirdly, that the liquefied gases, which are partly evaporated again in the process itself, are evaporated at a suitably reduced pressure of less than one atmosphere, and in quantities corresponding with the vapor tensions of the component parts of the mixture of fluids. For instance, as experiments by Dewar, Estreicher, Baile, Olszewski have shown¹ nitrogen has at -195° C. a vapor tension of 740 mm., oxygen a tension of 142 mm. By producing a re-

¹ Cf. *Zeitschrift für Komprimierte und Flussige Gase*, 2nd year, No. 12, p. 180.

duced pressure above a fluid the temperature is at once lowered, if sufficient heat is not admitted for the evaporation of the quantities of fluids sucked off. It is evident that—as in the present process the temperature, by producing a reduced pressure by means of a suction pump, can easily be lowered down to -200° or still farther, and as at these temperatures, the proportion of the vapors of both fluid parts is greater than $740/142$, therefore greater than 5—it is necessary to evaporate over five times as much nitrogen as oxygen. This proportion becomes greater with the lowering of the temperature and is according to Olszewski at -214° $60/3.8$, or 16. By producing a vacuum of 60 mm., which is technically easy, 16 times as much nitrogen

of the electrically indifferent slag at the low places, the higher lying places are subjected to the oxidizing influences of the atmosphere, while on the other hand, practice has shown that the accumulation of the slag at the lower lying portions causes a rapid destruction of the walls of the furnace. Attempts have



already been made to overcome these difficulties by superposing, over the primary winding, a short-circuited auxiliary winding in which a current is induced, during the operation of the furnace, in a direction opposite to that of the primary current and therefore counteracts the repulsion exerted upon the melting bath by the primary winding. But this arrangement results in a great loss of energy since the auxiliary winding must possess a very great resistance in order that the current induced in it will not be too strong.

The present invention has for its purpose to avoid the disadvantages recited and attains this purpose by providing means, which electrically opposes and restricts the current, which is induced in the auxiliary winding superposed over the primary winding, which means is so located in relation to the melting bath that it has no appreciable influence upon the equilibrium of the melting bath.

The accompanying illustration shows a preferred embodiment of the subject matter of the invention.

The inventor is Carl Grunwald, of Bredeney, Germany.

982,288. Preparation of Nitrogen Compounds.

This invention has reference to the manufacture of nitrogen compounds, such for instance, as lime nitrogen, etc.

More particularly, the invention relates to a process for the preparation of lime nitrogen without free carbon.

In preparing calcium carbide in the electric furnace, calcium oxid is treated with an excess of carbon, to form calcium carbide with the evolution of carbon monoxid. In order to prepare lime nitrogen, the patentees take calcium carbide and treat it in the presence of a flux and heat with nitrogen together with carbon dioxid, to form a resultant product containing approximately 35 per cent. of nitrogen. In the accompanying illustration 1 represents an electric furnace, wherein calcium carbide is produced by the action of an excess of carbonate of lime, or free calcium by reduction of calcium oxid by carbon, in the electric arc. In order to obtain lime mixed with the desired proportion of carbon, a limestone retort 2 is provided in which limestone mixed with coal in the desired proportion, according as calcium carbide or calcium is to be prepared, and burned to lime and carbon by heat from gas burners 3. The gas used is a mixture of carbon monoxid from the carbide furnace with air, air and acetylene or other suitable gas, so that a complete combustion of the gas is obtained in the retort 2, together

Fig. 1.

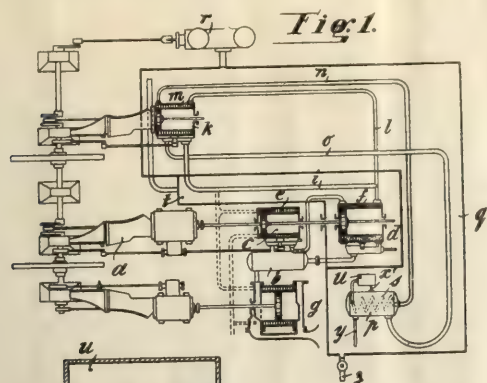


Fig. 2.

as oxygen will be evaporated, therefore leaving nearly pure oxygen. The process is therefore suited for separating out directly almost pure liquid oxygen, and by its distillation correspondingly pure gaseous oxygen.

The accompanying illustration shows a plant for the liquefaction of air according to this process.

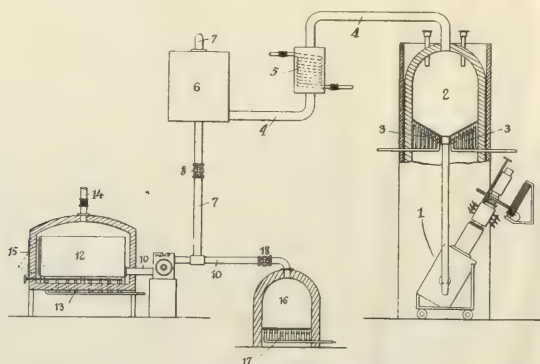
The inventor is Rudolf Mewes, of Berlin, Germany.

980,940. Electric Induction Furnace.

It has been observed in the operation of induction furnaces that the upper surface of the melting bath is inclined, in consequence of the electro dynamic effect exerted between the primary winding and the melting bath. For example, when the primary winding, or a portion thereof, is arranged concentric with the melting bath, repulsion takes place between the primary winding and the melting bath because the current induced in the latter flows in the direction contrary to that in which the primary current flows. Consequently the upper surface of the melting bath assumes such a position that the outer edge of the melting bath or that lying remote from the primary winding is higher than the inner edge. This exposure has disadvantageous consequences in that, on the one hand, owing to the accumulation

with the hydrocarbons which may be contained in the coal itself. From the retort 2 the lime and carbon are discharged into the electric furnace 1, either for producing calcium carbide or for producing pure calcium, according to the proportion of carbon used. The gaseous products of the combustion of the gas at the burners 3 and volatile constituents of the coal consisting of nitrogen, carbon dioxide and water, are conducted by a pipe, 4, through a drier, 5, to remove the water of combustion and thence to a tank, 6, containing lime water or some other means for separating carbon dioxide so as to leave pure nitrogen. The drier 5 removes the water, and the lime water tank 6 removes the carbon dioxide, so the remaining gas will consist of pure nitrogen, which passes from the tank 6, through a pipe, 7, containing regulating valve 8.

16 represents an ordinary limestone furnace, which may be heated by burners 17 for forming limestone carbon dioxide, which will pass through a regulating valve, 18, and thence by pipe 10 to the furnace 12. The calcium carbide is charged into the furnace through a suitable charging door as 15, and the furnace is heated by burners 13. Also, a flux of calcium fluoride or cryolite



or both is provided, and means for thoroughly mixing the gases with the melted carbide and flux. The flux does not react with the carbide, but has the function of promoting and assisting the reaction. Without the flux the nitrogen combines with the carbide, if at all, only on the outside of the particles, leaving the inside unchanged. The carbide is, so to say, indifferent to the combination with the nitrogen without the flux even though the temperature be raised as high as 1200-1500°.

The inventors are Einar Honoratus Meyer and Job Morten August Stillesen, of Niagara Falls Centre, Ontario, Canada.

982,945. Process of Manufacturing Cement.

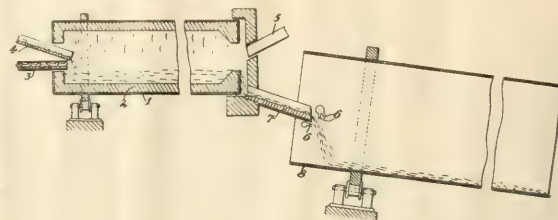
This invention relates to the process of manufacturing cement from furnace slag in which the slag receives an admixture of lime which is incorporated therewith, the mixture being subsequently disintegrated so as to form a highly cementitious granulated material which can be used as cement when properly ground.

The accompanying illustration shows apparatus which may be used in carrying out this process.

Ground lime is added to the liquid furnace slag in the proper quantities and thereafter the two materials are preferably intimately mingled and kept at a suitable temperature to cause the thorough incorporation of the various ingredients. This may be done in a suitable chamber or rotary kiln, the material being maintained in a fluid condition throughout the mixing process. The mixed material is then disintegrated in a uniform manner so as to form granulated material or cement clinker having highly cementitious properties.

In carrying out this process, a mixing furnace in the form of a horizontal or slightly inclined rotating cylinder or drum, 1, may be used, preferably having a suitable lining, 2, of fire-resisting material, and which may be arranged to be heated by

internal or external heating means. The molten furnace slag is run into this mixing furnace, as by the spout, 4, filling it up to the desired height, one-third of its height for instance. The proper amount of ground lime for forming the cement is also



introduced into the furnace by a screw conveyor, 3, or other distributing means, the furnace being rotated, of course, in the usual way. In order to maintain the proper temperature of the mixture during the rotation of the mixing furnace a supply of heated air from a burner or blast nozzle, as 5, may be provided which may be either forced into or conducted over the mixture in the furnace. In this way, an eddying motion may be set up in the mixture which will secure its homogeneity and also assist in desulfurizing it. Instead of air, oxygen or other gas or a mixture of gases may of course be employed for this purpose. The ingredients are thoroughly incorporated and combined in this way and their homogeneous condition secured by the rotation of the furnace, since by this means the material is carried up about half way on the ascending side of the furnace and then is thrown or falls back again; so that after treating the material in this way for the desired length of time during which it is kept in a molten condition to secure the better union of the various ingredients, the homogeneous liquid mixture may be discharged from the revolving furnace for further treatment.

For the purpose of disintegrating the material after having thus treated and made it homogeneous, the fluid mass may either immediately on leaving the furnace or at any subsequent period be granulated, as is well known in this art and a steam injector or other disintegrating means may be used for this purpose. An arrangement adapted to this end and forming a convenient supplement or attachment to the rest of the apparatus may comprise a jet tube or set of jet tubes, 6, arranged at the outlet chute 7, which joins the mixing furnace at the lower end and conveys the mixture in fusion into a rotating cylinder, 8, or the like, so as to enable one or a number of steam jets to be sent into the mixture running out of the furnace, such jet or jets having practically the same direction as the current of liquid mixture which by such means will become uniformly disintegrated or granulated. The granulated material thus obtained is a cement clinker having highly cementitious properties and forming cement when properly ground.

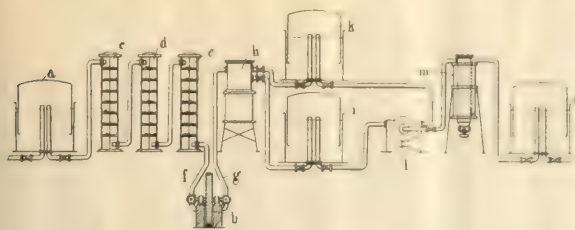
The inventor is Carl von Forell, of Hamburg, Germany.

983,199. Catalytic Synthesis of Methane.

This invention relates to a process for the catalytic synthesis of methane or a mixture of methane with other gases.

The object of this invention is to provide a process by which the sulfur impurities may be effectually removed and at the same time the cheapest of the commercial gases of the type of Mond gas and Duff gas and the like may be commercially treated for the production of methane, without there being any need to modify their process of manufacture. In carrying out this process the mixture of gases (which should be first freed from carbon dioxide) is cooled to the degree necessary in order to get the sulfur impurities into a solid form having little or no vapor tension the hydrogen passing off as a gas and being collected while the carbon monoxide, nitrogen, and methane will be liquid or solid. On allowing this latter mixture to evaporate carbon monoxide and nitrogen distil off first and are effectually separated

from the sulfur impurities. After this distillation process a certain quantity of the carbon monoxid obtained is mixed



with the hydrogen so that the hydrogen and carbon monoxide are

in the required proportions. This mixture is passed over nickel in the known manner. There should always be an excess of hydrogen over the theoretical quantity in order to prevent local heating of the metal. The amount of this excess depends on various circumstances, such as the speed at which the gaseous mixture is passed over the metal, and if nitrogen is present this acts as a diluent and assists in preventing local heating, and a smaller excess of hydrogen may be used than would otherwise be necessary.

The accompanying illustration shows a form of apparatus for carrying out the process.

The inventors are Fred Bedford and Charles E. Williams, of Sleaford, England.

EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

The Executive Committee of the Eighth International Congress has issued a preliminary announcement which gives the present status of the organization in the United States. Countries outside of the United States are urgently requested to form committees for the organized conduct of matters connected with the congress in which these countries are interested along the lines of the American organization.

The preliminary announcement contains:

Constitution and By-Laws; Requirements for Conduct of Congress; Rules on Papers and Publications; Rules on Sectional Procedure; Specialist Registration Bureau; Organization of the Eighth Congress; Officers and Executive Committee; Organizing Committee; Committee on Sectional Procedure; Committee on Coöperation; Sections and Subsections and their Executive Committees; Local, Hotel, Entertainment and Transportation Committees.

After a preliminary statement covering the history of the development of the eighth congress, the pamphlet describes the organization and purpose of the various committees, sections and subsections.

A committee on coöperation has been established in order to secure beneficial coöperation and affiliation between the eighth congress and other scientific or professional bodies meeting in, or near New York or Washington at, or about the time of the convening of the eighth congress.

The President of the United States has shown his deep interest in the object and purposes of the eighth congress by consenting not only to act as patron, but also to preside at the opening meeting which is to be held in Washington, on Wednesday, September 4, 1912. The President of the United States has also caused invitations to be sent to all the governments of the world to take part in the deliberations and the work of the congress.

The chemists, therefore, owe, not only to their science, and to their profession, to exert every effort to make the International Congress of Applied Chemistry completely successful, but also owe it to their own country and their own Government to use every means in their power to see that the interest in their country is properly and fully represented.

The constitution and by-laws governing the congress are printed in full, and provide for the control of the organization and its various committees. The membership of the various committees is given in full.

The organizing committee is composed of representatives of all the affiliated societies, and in addition to that, a body of representative scientists from every State in the Union.

The technical work of the congress is divided under sections and subsections as follows:

ANALYTICAL CHEMISTRY, *President*, W. F. Hillebrand, Bureau of Standards, Washington.

INORGANIC CHEMISTRY, *President*, Charles L. Parsons, New Hampshire College, Durham, N. H.

METALLURGY AND MINING, *President*, Joseph W. Richards, Lehigh University, Bethlehem, Pa.

EXPLOSIVES, *President*, Charles E. Munroe, George Washington University, Washington.

SILICATE INDUSTRY, *President*, A. S. Cushman, Tibbs Building, Washington.

ORGANIC CHEMISTRY, *President*, M. T. Bogert, Columbia University, New York.

COAL TAR COLORS AND DYESTUFFS, *President*, Herman Metz, New York.

INDUSTRY AND CHEMISTRY OF SUGAR, *President*, W. D. Horne, Yonkers, N. Y.

INDIA RUBBER AND OTHER PLASTICS, *President*, L. H. Baekeland, Yonkers, N. Y.

FUELS AND ASPHALT, *President*, David T. Day, United States Geological Survey, Washington.

FATS, FATTY OILS AND SOAPS, *President*, David Wesson, New York.

PAINTS, DRYING OILS AND VARNISHES, *President*, Maximillian Toch, New York.

STARCH, CELLULOSE AND PAPER, *President*, A. D. Little, Boston.

FERMENTATION, *President*, Francis Wyatt, New York.

AGRICULTURAL CHEMISTRY, *President*, Frank K. Cameron, Department of Agriculture, Washington.

HYGIENE, *President*, W. P. Mason, Rensselaer Polytechnic Institute, Troy, N. Y.

PHARMACEUTICAL CHEMISTRY, *President*, Joseph P. Remington, Philadelphia.

BROMOTOLOGY, *President*, W. D. Bigelow, Department of Agriculture, Washington.

PHYSIOLOGICAL CHEMISTRY, *President*, John J. Abel, Johns Hopkins University, Baltimore.

PHOTOCHEMISTRY, *President*, W. D. Bancroft, Cornell University, Ithaca.

ELECTROCHEMISTRY, *President*, William H. Walker, Massachusetts Institute, Boston.

PHYSICAL CHEMISTRY, *President*, W. R. Whitney, Research Laboratory, General Electric Co., Schenectady, N. Y.

LAW AND LEGISLATION AFFECTING CHEMICAL INDUSTRIES, *President*, The Hon. Edward D. White, Chief Justice of the Supreme Court of the United States, Washington.

POLITICAL ECONOMY AND CONSERVATION OF NATURAL RESOURCES, *President*, J. A. Holmes, Bureau of Mines, Washington.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF FEBRUARY.

For Full List of Weekly Quotations, see "Oil Paint & Drug Reporter."

Organic Chemicals.

Acetanilid.....Lb.	20 ¹ / ₂ @	23
Acetone (drums).....Lb.	14 ¹ / ₂ @	16
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	1.80 @	1.93 ¹ / ₃
Acetic Acid (28 per cent.).....C.	1.65 @	1.78 ¹ / ₃
Acetate of Lime (gray).....C.	1.75 @	1.80
Acetate of Lead (brown, broken).....Lb.	7 ³ / ₄ @	8
Aniline Oil.....Lb.	11 ¹ / ₂ @	11 ³ / ₄
Benzoic Acid.....Oz.	11 ¹ / ₄ @	12
Boric Acid, crystals.....Lb.	7 @	7 ¹ / ₂
Carbon Tetrachloride (in drums).....Lb.	8 ¹ / ₈ @	12
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (in drums).....Lb.	8 ¹ / ₆ @	9 ⁵ / ₆
Citric Acid (domestic).....Lb.	38 ¹ / ₂ @	39
Camphor (refined in bulk).....Lb.	.. @	43
Dextrine (imported potato).....Lb.	5 ¹ / ₂ @	7
Dextrine (domestic corn).....C.	2.12 @	2.28
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 ¹ / ₂ @	9 ¹ / ₂
Glycerine (dynamite).....Lb.	23 ¹ / ₂ @	25
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7.20 @	7.75
Pyrogallie Acid (bulk).....Lb.	1.00 @	1.05
Paraffine (crude) 120 @ 122 m. p.....Lb.	3 @	3 ¹ / ₄
Paraffine (refined), domestic 120 @ 122 m. p.....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	1.37 @	1.53
Starch (potato).....Lb.	4 @	5 ¹ / ₄
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 ⁷ / ₈ @	5 ¹ / ₄
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	29 ¹ / ₄ @	29 ¹ / ₂

Inorganic Chemicals.

Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (in drums) 16°.....Lb.	2 ³ / ₄ @	3
Ammonium Chloride, gray.....Lb.	6 ¹ / ₃ @	6 ¹ / ₄
Arsenic, white.....Lb.	2 ¹ / ₈ @	2 ⁵ / ₈
Ammonium Carbonate, domestic.....Lb.	8 @	8 ³ / ₄
Aluminum Sulphate.....Lb.	9 @	10 ³ / ₄
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2.25
Barium Nitrate.....Lb.	5 ¹ / ₂ @	6 ¹ / ₂
Borax, crystals in bags.....Lb.	3 ¹ / ₂ @	4
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.25 @	1.30
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 @	4 ¹ / ₄
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	83 @	85
Chalk (light precipitated).....Lb.	4 ¹ / ₂ @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (in bags).....C.	62 ¹ / ₂ @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 @	8 ¹ / ₂
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	74 @	76 ¹ / ₃
Nitric Acid, 36°.....Lb.	3 ⁷ / ₈ @	4 ¹ / ₄
Nitric Acid, 42°.....Lb.	4 ⁷ / ₈ @	5 ¹ / ₄

Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25
Plaster of Paris.....C.	1.35 @	1.70
Potassium Bromide.....Lb.	25 @	28
Potassium Permanganate (bulk).....Lb.	9 ⁷ / ₈ @	11
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals, f. o. b. works.....Lb.	8 ¹ / ₄ @	9 ¹ / ₂
Potassium Nitrate (crude).....Lb.	4 ³ / ₄ @	5
Potassium Bichromate, 50°.....Lb.	7 ³ / ₈ @	7 ³ / ₄
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	62 ¹ / ₂ @	65 ¹ / ₃
Salt Cake (glass-makers).....C.	66 ² / ₃ @	80
Silver Nitrate.....Oz.	34 ⁵ / ₈ @	37 ¹ / ₈
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 ¹ / ₂ @	5
Sodium Chlorate.....Lb.	8 ¹ / ₄ @	9 ¹ / ₂
Sodium Bicarbonate (English).....Lb.	2 ³ / ₄ @	3
Sodium Bichromate.....Lb.	5 ³ / ₈ @	5 ³ / ₄
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 ¹ / ₂
Sodium Hydroxide, 60 per cent., f. o. b. works.....C.	1.85 @	1.90
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.	7 @	10
Sodium Nitrate, 95 per cent., spot.....C.	.. @	2.10
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 ³ / ₄ @	10
Strontium Nitrate.....Lb.	7 ³ / ₈ @	7 ³ / ₄
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	90 @	1.00
Talc (American).....Ton	15.00 @	25.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	14 ³ / ₅ @	12 ⁵ / ₆
Tin Oxide.....Lb.	44 ¹ / ₃ @	46 ¹ / ₃
Tin Chloride (36°).....Lb.	32 @	33 ¹ / ₄
Zinc Chloride (granulated).....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Zinc Sulphate.....Lb.	2 ¹ / ₄ @	2 ¹ / ₂
Zinc Dust.....Lb.	6 ³ / ₄ @	7

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 ¹ / ₂
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	10 @	20
Corn Oil.....C.	7.15 @	7.20
Cottonseed Oil (crude), f. o. b. mill.....Gal.	44 @	44 ⁵ / ₆
Cylinder Oil (light, filtered).....Gal.	19 ¹ / ₂ @	20
Japan Wax.....Lb.	9 ¹ / ₄ @	9 ¹ / ₂
Lard Oil (prime winter).....Gal.	1.05 @	1.18
Linseed Oil (raw, city).....Gal.	96 @	97
Linseed Oil (double-boiled).....Gal.	98 @	99
Paraffine Oil (high viscosity).....Gal.	23 ¹ / ₂ @	24
Rosin Oil.....Gal.	— @	36
Spindle Oil, No. 1.....Gal.	14 @	14 ¹ / ₂
Stearic Acid (double-pressed).....Lb.	11 @	11 ¹ / ₂
Sperm Oil (bleached winter) 38°.....Gal.	87 @	90
Tallow (acidless).....Gal.	69 @	70
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum.....Lb.	21 @	21 ¹ / ₂
Antimony.....Lb.	7 ¹ / ₄ @	7 ³ / ₄
Bismuth.....Lb.	1.80 @	1.90
Copper (electrolytic).....Lb.	12 ¹ / ₂ @	12 ¹ / ₃
Copper (lake).....Lb.	12 ¹ / ₂ @	12 ³ / ₄
Lead.....Lb.	4.4 @	4.5
Mercury.....Lb.	61.3 @	61.5
Nickel.....Lb.	40 @	45
Platinum (refined).....Oz.	38.50 @	39.00
Silver.....Oz.	51 ³ / ₈ @	51 ⁷ / ₈
Tin.....Lb.	37 ³ / ₄ @	43 ³ / ₄
Zinc.....Lb.	5.4 @	5.6



VIEW OF CHEMISTS' BUILDING FROM HOTEL BELMONT. MURRAY HILL HOTEL AT THE LEFT.

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CHEMISTS' BUILDING.

The opening of the new Chemists' Building in New York City is an event of national, rather than merely local significance, and the committee in charge has done its duty by seeking to express this fact in the programme of the opening exercises. The social comforts of the Chemists' Club are but an incident in the general scheme, and, in fact, the physical transfer of that organization from its present quarters to the splendid home now provided for it must, necessarily, await the completion of its furnishings, after the building itself was declared ready for occupancy. Hence, the Club's festivities were subordinated to the dedication ceremonies of the building, when due emphasis could be laid upon the serious aims of the enterprise, and to the scientific meetings, under the auspices of the local sections of our Society, the American Electrochemical Society and the Society of Chemical Industry. It will not be the fault of the speakers at these meetings, if the general public fails to grasp the importance of chemistry in our industrial development, and also as a branch of pure science. We ourselves, and, especially, those of us who do not dwell in New York itself or its immediate vicinity, might well take this occasion to reflect upon the practical significance of this undertaking.

Nobody can review the history of American progress during the past twenty-five years without recognizing how much more intimately chemistry is enmeshed in the general economic and sociological texture than a quarter century ago. Then, the American student who went beyond the general chemical courses prescribed for all freshmen and sophomores did so as a preparation for medicine or some other recognized profession, or with the definite purpose of entering an academic career. The possibility of establishing himself as an independent chemical analyst or expert was certainly never placed before the student; and the works chemist, in the eyes of the industrial world, was held in the sort of regard which may be likened to Lincoln's estimate of the value of brigadier-generals, when he remarked, on hearing that a Confederate raider had cut out a baggage train and captured three generals, "I can make a brigadier any day, but mules cost money." Under such conditions, chemistry as a profession could have slight standing, and the gregarious needs of its votaries were amply met by the annual "meetings" of Section C of the American Association for the Advancement of Science, and by occasional local gatherings. The reorganization of the American Chemical Society on a national basis, in June, 1890, presaged the change which seems to have followed the World's Fair at Chicago. We need not inquire too closely whether the lean years

following the financial crisis of 1893 caused manufacturers to appreciate more fully the value of chemical control of their processes, or whether the exhibits of German and other foreign manufacturers, coupled with the demonstration of the World's Chemical Congress, attracted the attention of the American public to the possibilities of the development of a true chemical industry. Whatever share these or other influences may have borne, the result may be strikingly shown in a circumstance connected with the opening ceremonies of the Chemists' Building. In the preface to Volume XII of the *Journal of the American Chemical Society*, the editor estimated the number of chemists available for the newly-formed New York Section at two hundred; twenty-one years later, with duplicates eliminated, thirteen hundred invitations were sent out to the *enrolled* members of the New York local sections of the three large chemical societies.

Of course, in this phenomenal development of the chemical profession, America is merely catching up with European progress, not leading it. The enormous attendance at the recent Triennial Congress of Applied Chemistry was well calculated to astonish the non-chemical world; and if the initiative taken at Chicago in 1893 toward convening these congresses is to our credit, the contrast between the two hundred and fifty men then in attendance and the chemists who will crowd New York in October, 1912, will convince America not only that progress has been made, but also that still greater advances must be accomplished here, to keep pace with chemical industry abroad. The American Chemical Society would not fulfil its duty toward its membership by holding occasional meetings and publishing the proceedings thereof; it must afford them a means for the prompt publication of their researches, as well as for their information upon the world's progress in pure as well as applied science; its journals must be the link which binds the isolated worker to his profession. But, there are still other needs; the relations of the professional chemist toward the industries must be established on a sounder basis; the elimination of wasteful methods of manufacture through chemical control must be advocated more forcibly and pervasively; chemical industry must coöperate more closely toward the furthering of mutual interests, toward the establishment of more satisfactory manufacturing conditions, from the legal, as well as the hygienic and economic aspect; aids must be devised for the furtherance of research, along industrial as well as purely scientific lines.

All of these ideas have been expressed at one time or another by the promoters of the American Chemical Society, and they were also in the minds of the founders of the Chemists' Club of New York, which for the past twelve years has maintained, at considerable pecuniary sacrifice on the part of its members, an organization in which the social features were infinitesimal as compared with the furtherance of the above-named objects. The new Chemists' Building represents the concrete embodiment of these ideals, and the par-

ticipants in the VIII International Congress will find established in New York City the first building devoted to the furtherance of chemical science and industry by *all* those means which are not distinctly pedagogical. This is a somewhat bold assertion, but it will bear analysis.

It is needless to descant upon the advantages to be derived from a well-equipped social club, which affords an attractive gathering-point for the local chemist, as well as housing accommodations for the nonresident member. But it might be well to bear in mind that the industrial chemist usually visits New York for professional consultation, or for the discussion of important business propositions; the technical library is an indispensable tool which he can now employ without quitting his shelter. Indeed, if a problem arises suddenly that requires experimental test, the laboratory in which to try it can be obtained with no more formality than that needed for engaging a bedroom. For quite a number of years, the Chemists' Club has made it an object to promote the interests of young chemists, as well as those of the manufacturer, by maintaining a professional employment bureau, which was chiefly hampered by the lack of a permanent office. Could this not be established in the new Club-house in such a manner as to greatly facilitate the establishment of communication between the dispenser and seeker of employment?

The existence of a complete building, devoted solely to the interests of the chemists, will probably be the best demonstration to the American public of the importance which this profession has now assumed from the technical standpoint. The consulting chemist, housed in laboratories for his own use, can well expect greater consideration than the man who is obliged to conduct his work in a ramshackle rookery, or, at best, in an out-of-the-way corner of a general commercial building. But, apart from any mere question of ostentation, the business man or manufacturer frequently fails to seek chemical advice, on questions of real importance, from ignorance of the manner of setting about it and sheer indolence in ascertaining it. Many do not even seem to know that there is such a man as a consulting chemist. May not some eyes be opened and some extravagant waste of natural resources be avoided, by persistent efforts of the manager of this central home of chemistry, and the rule of thumb be replaced by the rule of scales?

The American Chemical Society has gradually accumulated a library of considerable magnitude, which has been deposited of recent years with the Chemists' Club, which organization has acquired, by gift and purchase, many volumes of its own. But the shelf-space has been so limited, that but few of the books were accessible and even then could only be consulted under unfavorable conditions. In the magnificent "Chandler Hall" the entire library will be available for consultation at all reasonable hours. But it is also planned to establish a collection of duplicates, to be loaned freely to reputable chemists throughout the country. Here again, the provision of a suitable

working-place will serve not merely the local interests, but perhaps even more effectively, the scattered outposts of chemical endeavor.

One of the chief disadvantages under which the American investigator labors is the difficulty of obtaining research material. The German or French experimenter can obtain, within twenty-four hours, a specimen of virtually every chemical substance that is in the market: the American depends upon the stock of two or three importers, which must necessarily be limited in regard to the rarer preparations, or he must import directly, with inevitable delays in transit and especially at the custom-house. The Chemical Museum is planned to obviate this, by keeping as complete a collection of substances as possible, in relatively small quantities, it is true, which will be loaned to investigators who require material for preliminary investigation. Such a preliminary test may go far towards determining the course of a research and deciding whether it is worth the chemist's while to procure larger quantities. But, the projectors also hope to induce the American chemists to deposit with the Museum samples of all new substances prepared in their researches, to serve a similar purpose as do type specimens in a Museum of Natural History, as standards of comparison for future investigators. Here we should have the first chance of facilitating chemical research in America by coöperation, instead of by subsidizing individual investigations. It will take some time to perfect the plans; but if it can be accomplished, the student in a Rocky Mountain college will be within as easy reach of his materials as his fellow in a large city of the East.

We have detailed some of the more striking advantages which the new building is expected to confer upon the chemical profession as a whole, as well as upon its individual votaries; is it an exaggeration to characterize the constitution of the Chemists' Building Company itself as a new era in the chemical industry of our country? In scanning the list of shareholders, we find representatives of nearly every important concern, or even the larger companies themselves; but that this is not a "trust," in the sense so obnoxious to the yellow journalist, is demonstrated by the conditions of the partnership. No shareholder can receive more than 3 per cent. dividends and the surplus cannot, under any circumstances, accrue to his benefit within the next fifty years. This association, therefore, is not for individual profit, but for the *raising of the standards of chemical industry and research in the United States*. If we recognize what the Verein zur Hebung der Chemischen Industrie, founded by Hofmann and Werner Siemens, has done for Germany, we may well hope for further fruits of this initiative here. Perhaps this building will house joint laboratories for the solutions of questions affecting all manufactures alike; or experimental stations for the study of natural products not yet utilized; or a coöperative bureau of standardization for analytical methods; or a national welfare bureau for employees in chemical factories. This building does not owe its erection to some benevolent demigod,

extending his protecting wing over people unable to care for themselves; it is a building by the chemists, of the chemists, and for the chemists. May it ever serve as an exemplar of unselfish patriotic coöperation!

HISTORICAL.

The history of the movement which led up to the dedication of the first building in the world built, owned and occupied exclusively as a social, scientific, and business centre for the Chemical Profession, is filled with human interest and shows a devotion and self-sacrifice to the interests of that profession which presages great and rapid future development.

The early vicissitudes of the chemical societies in New York are still fresh in the minds of many of the older members. In 1880 a few chemists used to meet in a room in the old University building in Washington Square. Here among the litter of journals, books, and unopened or partly opened packing boxes, they held their scientific meetings and discussed plans for the future of the profession. The woodshed is frequently referred to as the proper starting point for distinction and success. This room, "furnished with junk", in the old University was the "woodshed" of the "Chemists' Club Movement."

The attendance of these meetings soon outgrew the capacity of the original quarters, and Dr. Doremus placed at their disposal his lecture room in the City College, then at 23d Street and Madison Avenue. The chemists felt the natural effects of decentralization, however, and in 1895 appointed a committee with Professor Breneman as chairman to find a floor or two in an old house where they might establish the library and meeting rooms under more favorable conditions. No result came from this on account of the limited means available. Dr. McMurtrie and Dr. Hale labored with indefatigable energy to build up the membership of the Society and the need for permanent headquarters increased proportionally.

About this time Dr. McKenna discovered through the medium of a newspaper advertisement a house for Club purposes in West 55th Street. He went to see it, realized its possibilities, visited the agent, acquired a most favorable option, and placed the matter before the officers of the Society.

A special meeting, called to discuss the plan, was held in the auditorium of the building in question. Professor Chandler offered to lend the money for the first year's rent, and was guaranteed against loss by 100 members in case the project failed. The building was furnished by subscription, and the first Chemists' Club was launched in September, 1899, at 55th Street near Sixth Avenue.

The plan was a success from the start. The several chemical societies and other scientific organizations held their meetings in the auditorium, and the place soon came to be the centre of all important scientific gatherings in New York City.

The rapid growth of the profession soon made it evident that the 55th Street house would not accommodate the library, the meetings, and the other needs of the Organization.

Dr. Toch became President of the Club in 1907, and in his retiring address, after reviewing the success of the Club, he announced that the time was ripe and he was ready to undertake to develop ways and means for the chemists to build a larger and better house of their own. Professor Loeb became interested, and suggested a plan to include special laboratories, offices, and other accommodations for professional chemists. Professor Loeb furthermore gave tangible form to the enterprise by offering to subscribe \$50,000 which he subsequently increased to \$75,000. Dr. Nichols and his associates subscribed \$50,000. A Finance Committee was organized and various plans were discussed. In 1908 the old Tilden Club Building at 74th Street and Broadway was offered for sale, and was being considered by a committee, when the present site at 52-54 East 41st Street came to the attention of Dr. McKenna, who again realized an opportunity and appreciated its advantages as a central location and arranged for its purchase.

The building was planned and erected under the supervision of the Directors of the Chemists' Building Company, Dr. Morris Loeb, Dr. Charles F. Chandler, Albert Plaut, W. H. Nichols, Jr., and Dr. L. H. Baekeland.

The steady progress of the Chemists' home in New York, from the single room in Washington Square furnished with packing cases and strewn with books and journals, to the handsome eleven story building at Fourth Avenue and 41st Street, with its auditorium, library, museum, laboratories, offices, social rooms, living quarters and restaurant will always be intimately coupled with the history of the development of the profession, and marked by the unselfish devotion of these and many other loyal hard-working men to the interests of chemists, whether they be native or foreign, young graduates, or men years in the service of the profession.

A NEW DYEING INDUSTRY TO BE ESTABLISHED.

The Bradford Dyers' Association, a very large English corporation, which practically controls the great bulk of dyeing in the United Kingdom, has definitely

decided to establish a branch works in this country. This has been brought about in one sense by the operation of the tariff which has put a higher rate of duty on dyed and finished cloth than on the unfinished material. In another sense it has also been brought about by the increasing competition of American mills in the production of novelties which have hitherto been specialties of the Bradford Dyers' Association. The English Corporation has quietly bought up about 800 acres of land along the Pawcatuck River at Niantic, R. I. Their purchases include also the small plant of the Niantic Dyeing Co., together with flowage rights, docking privileges, and railroad facilities. There is every indication that a large plant is to be erected in the immediate future with the idea of developing a general commission dyeing business on a large scale. The Bradford Dyers' Association has now forty-six plants in operation in England, and as the company is backed by almost unlimited capital, and has under its control a large number of processes and valuable specialties, there is no doubt but that its influence will be largely felt in this phase of American industry. It is expected to have a unit plant in operation at Niantic by the coming summer; that is to say, a plant of sufficient size to dye and finish about 1000 pieces per day. As the business develops and grows this unit plant will be duplicated as often as conditions demand. As the circumstances and organization of the American textile industries are somewhat different than in England, it is a question open to considerable discussion as to whether this move of the Bradford Dyers' Association will prove to be a successful one. One factor which has probably hastened the determination of the English firm is the circumstance that a large French dyeing corporation has also decided to enter the American field by the erection of extensive plants in this country. It is to be hoped that the Bradford Dyers' Association will have a more successful venture than was the case with the earlier experiences of the British Cotton and Wool Dyers' Association, in their endeavor to establish a branch of their yarn-dyeing industry in America.

J. MERRITT MATHEWS.

THE CHEMISTS' BUILDING.

By E. L. ELLIOTT, Editor *Illuminating Engineer*.

It is a question which of the two sciences whose origin extends back into the ages possesses the richer lover of historical romance, astronomy or chemistry. When in the dawn of civilization man began to wander from place to place, seeking to destroy or to escape destruction, he learned to use the stars as guide posts, and his imagination discovered in the heavens the outlines of the beasts of the field and the other forms of nature with which he was most familiar; and so he came to believe that his entire destiny lay within the powers of this mysterious dome above. The race of astrologers is even not yet extinct, while the modern science of astronomy has mapped and weighed the heavens with well nigh superhuman exactness.

The beginnings of chemistry came later, when man had learned to extract some of the commoner metals and turn them to his use; and when gold became the substance and the symbol of wealth, the search for methods of producing it from the baser metals afforded a field of infinite possibilities, with the motive of cupidity for all that wealth signifies as an instigator and promoter of the work. Added to this was the equally powerful incentive of discovering a means of escaping sickness and death. The universal belief in immortality is the child of a wish to defeat the inevitable course of nature, to the end that man may enjoy perpetually the delights of youth. To possess youth forever and gold at will! Who would not strive to accomplish this end? The modern science of chemis-



MAIN ENTRANCE FROM THE OFFICE.



AUDITORIUM FROM THE ROSTRUM.



SOCIAL ROOM.



TRUSTEES' ROOM.

try thus has an origin quite as romantic and fanciful as its sister science of astronomy.

Today we think of the alchemist as a misguided philosopher of the Middle Ages, hopelessly striving to achieve the impossible, but who, building better than he knew, laid the foundations of the science of chemistry, which in its benefits to mankind at least equals all the inventions and improvements in the mechanic arts. Nor need we turn to Europe or the Dark Ages to find an example of the popular distrust of the "black art" of alchemy. The first chemical laboratory ever instituted in this country was practically a dungeon, being entered by a trap door from the top, and occupying a subterranean room; such was the laboratory of Prof. Silliman, of Yale.

It has been well said that the progress of science has proceeded with an accelerated velocity, a year now equaling the progress of a previous decade, and a decade surpassing the progress of a previous century. Within the span of a single human life we have progressed from the cellar of Prof. Silliman to the magnificent modern fire-proof structure of this Club; and the Club itself has but barely reached its majority, and the building in which it is now housed was only a bold conception of one of its honored presidents but four years ago.

In exterior design the building may best be characterized as modern American, the architecture being an adaptation of the best traditions of building to the necessities and conditions of modern construction and requirements. The facade is of light buff sandstone treated in a simple and wholesome manner without any effort at conspicuous decoration, the general motive being classical. The balcony at the top and the metal work about the windows is finished in verd bronze, giving a most pleasing harmony of color.

The general plan of the building is unique in combining all of the social requirements of a Club with the practical utilitarian features of the professional chemical laboratory. These two features, while intimately combined, are at the same time entirely separated for practical purposes. Thus, the auditorium and the laboratories can be reached without in any way intruding upon the portions of the building devoted to club use, while on the other hand, the Club sections of the building are in direct communication with the business portion. A detailed description of the building by floors will make this arrangement clear.

The first, or street, floor is occupied by the lobby and office of the Club, and the auditorium. The lobby occupies the front section, and is entered directly from the street. As you enter, the office is at the immediate left, a handsome fire-place at the right, and the main hallway leading to the auditorium in the rear. At the left of this hallway is the main stairway to the various club-rooms above, with a coat-room at the entrance to the auditorium. The walls of the lobby are finished in plain oak paneling in antique finish, with pilasters of freestone; the ceiling is white with simple plastic decoration of conventional classic design. The auditorium is two stories in height with a gallery in the rear. It has a seating capacity of 300 on the

main floor and 50 in the gallery. The stage is lighted by a skylight, and has preparation-rooms on either side. Removable tables are provided, so arranged that they can be readily connected to supply water, gas, electricity, compressed air, and vacuum; when not required for experimental or demonstration purposes they can be removed, and the stage left entirely free. A panel at the rear of the stage is finished white to serve as a stereopticon screen, and a stand for the lantern, with electric current at hand, is provided in the gallery. A blackboard, arranged so that it can be drawn up into position for use or lowered when the screen is required for lantern views, is also provided.

An ample hallway leading direct from the street to the auditorium extends along the right side of the building, so that it is possible to close the auditorium entirely from direct communication with the lobby when desired, thus making it available for use for other purposes without in any way encroaching upon the privacy of the club members. The elevators to the upper floors are also reached directly by this hallway, which opens into the lobby, thus permitting the laboratories and private rooms to be reached with equal facility either through the lobby or from the street direct.

The gallery of the auditorium is reached from a mezzanine floor, which is devoted to private offices. Laboratories are provided in the section between the stairway and the auditorium.

The second floor is given over to the dining-room and the social room. The latter occupies the entire front section of the building, having large windows on the street side, and a handsome fire-place at either end. The general character of the architecture has been carefully preserved in this as in the other features of the interior treatment; there is simple elegance rather than ornate decoration. The woodwork is of mahogany; the side walls are covered with tapestry in natural color background with a simple figure in old blue; the ceiling is paneled in very low relief, and given a cream tint. As the rooms were not furnished at the time of the dedication the photographs necessarily show them in this condition, and so, while giving an idea of their spaciousness and general appearance, the imagination must supply the air of homelike comfort which only a furnished and used room can possess.

The dining-room occupies the rear section of the floor, and is finished in mahogany, with walls of dull red. The ceiling is perfectly plain and of a light cream tint. At this height the rear of the building has no immediate obstruction, so that the dining-room is beautifully lighted by large windows facing the south. This gives the cheerfulness of such sunshine as is vouchsafed us in the winter months, while in the summer the projecting roof of the auditorium affords an open air café.

A dining-room necessarily implies a kitchen, and this necessity has been most carefully provided for in a room of ample dimensions and equipped with every modern facility known to the culinary art. There is a particularly close relation between chemistry and cooking; but whether the analytical propensities of the chemists are sufficiently perfected to enable

them to prepare viands synthetically remains to be seen. It is a fairly safe prophesy that the savants of the test tube and wash bottle will be satisfied to follow Sancho Panza's formula in thier tests of the puddings.

On the third floor the front section has been set apart for the library. The finish here is quartered oak with plain walls. The bookstacks are arranged along the inner wall, leaving the front portion by the windows for the reading tables. Dr. C. F. Chandler has signified his intention of donating his private library to the Club for immediate use. This benefaction will afford a splendid foundation for a very complete chemical library. It is worth mentioning that the gift comes from a teacher who may rightfully be called the Dean of Chemistry in this country, and a fine life-sized bronze of Dr. Chandler by Hartley furnishes a fitting and striking figure in this room, which is to be known as Chandler Hall.

The rear section of this floor contains a room which is to be used as a museum and reference room. It is finished in quartered oak and is left without decoration. Adjoining this there is a small room which is perhaps the most unique feature of the entire building. The official name of this is the Trustees' Room, but it has already acquired the facetious title of "The Chapel." The room has been designed to represent the den of the ancient alchemist. There is a "high-arched, vaulted ceiling" under which the imagination can readily depict Dr. Faustus himself ranging over the field of human knowledge, to find himself at the end no wiser than before. A Gothic window with roundels set in leaded glass admits subdued daylight, while at the opposite end is a crude furnace, ready to receive the alembic and the crucible. A small metal lantern of mediaeval pattern hangs from the ceiling at this end, while the traditional salamander, defying history by grasping modern electric lamp bulbs in his claws, swings from chains at the other end. An iron chest of ancient design, with ponderous key, occupies a corner of the room, and doubtless contains the secret of the philosopher's stone and the elixir of life. A massive oaken table occupies the center of the room, and suggests the parchment tome in black-letter, but alas is more likely to witness the anachronism of a stenographer's notebook.

The fifth and sixth floors are divided into single rooms and suites for the use of the Club members and their guests. In the furnishing of these some genius hit upon a very happy idea, *viz.*, to have a number of the alumnae of colleges that are well represented in the membership each furnish a room or suite. The following institutions have accepted this idea: University of Pennsylvania, New York University, Cornell University, Massachusetts Institute of Technology, Yale University, College of the City of New York, University of Michigan, University of Virginia, Johns Hopkins University, German Universities, Swiss Universities, British Schools and Universities, University

of Tokio, and the City of Chicago. The walls are hung with views of the familiar scenes on the campus and in the buildings, together with the emblems that are dear to the heart of the college man. Thus, added to all the comforts to be found in the best modern club or hotel is the memory of the good old college times, when it was considered a mark of special prowess to blow the gas pipes in the chemical "lab" full of air, or produce reactions between NH_4OH and HCl that were not prescribed in the course, and which resulted in a general clouding of the vision, or perhaps to perfume the instructor's overcoat with valerianic acid.

The remaining six floors of the building are designed for laboratory use. All the facilities required by the chemist are provided, and the spaces so arranged that they can be subdivided to suit the exact requirements of the tenants. The floors are of cement, and are made continuous with the baseboard, and are supplied with a drain at either corner so that a stream of running water could be left on the floor continuously without doing the slightest damage to the floor itself or the room beneath. There are arrangements for hoods with separate outlet and inlet openings reaching to the roof. These rooms offer the combined advantages of complete modern equipment, unsurpassed light and ventilation, the most central location in the city, and immediate connection with an organization representing the entire chemical profession of the country. It is small wonder therefore that they have been eagerly taken up by consulting and professional chemists.

A feature deserving of special mention is the complete equipment, including all the regular chemical apparatus, of two small laboratories, which will be let to competent chemists who wish to conduct temporary experiments or demonstrations. These are on the ninth floor, and are known as the Robert Bunsen and the Wolcott Gibbs laboratories. The difficulty of securing such facilities is a common experience with the chemical departments of universities, and with those who have found it necessary to make demonstrations of new processes or products to prospective investors. If there ever was a case of "filling a long-felt want" this is certainly one.

The building is served by three elevators which immediately reach all offices and laboratories, and also by stairways at each side.

The building throughout shows the utmost care and thought in the planning of every detail. It should perhaps rather be called a growth than a plan, for the arrangement and the construction have received the unremitting thought and attention of a number of the best chemists, in connection with the architects, Messrs. York and Sawyer. But an original conception worked out to so complete a success as this is worth a lifetime of labor and thought. The Chemists' Club stands today as the most unique building of the kind in this or any other country.

ORIGINAL PAPERS.

PRELIMINARY REPORT ON THE TERNARY SYSTEM
CaO-Al₂O₃-SiO₂. A STUDY OF THE CONSTITUTION
OF PORTLAND CEMENT CLINKER.

By E. S. SHEPHERD AND G. A. RANKIN

With Optical Study by FRED E. WRIGHT.

Received February 24, 1911.

Two earlier papers from this laboratory¹ having prepared the way for a systematic study of the ternary systems, we desire to present the results thus far obtained with the interesting oxides, lime, silica and alumina.

It would be better for a number of reasons to delay publication until a final paper could be presented, but the active interest of technical men in the Portland cement portion of the diagram, as well as the necessarily time-consuming nature of the observations, seems to justify offering a preliminary report without further delay. To fix the position of all the fusion surfaces of this diagram will require considerably more time, but it is hoped that the facts thus far obtained will suffice as a starting point for those primarily interested in technical cement problems.

It will be well to begin by reviewing briefly the results obtained in the study of the binary systems, partly in order that we may have clearly before us the conclusions upon which the present work is based, and partly because the work with three components has revealed some important new developments in the relations which obtain in the two-component systems.

Lime-Silica Series (Fig. 1).—It will be recalled that pure lime and pure silica were found to combine to form two definite compounds, the metasilicate (CaO·SiO₂) and the orthosilicate (2CaO·SiO₂). In mixtures of pure lime and silica, no trace of the generally accepted tricalcic silicate (3CaO·SiO₂) was found, nor of a compound of the type 4CaO·3SiO₂, which is familiar to mineralogists under the name äkermannite. More recently, we have found that a small addition of alumina is sufficient to bring out the tricalcic silicate, which proves to be a compound with peculiar properties and limitations which will be discussed presently, just as Vogt has found² that the addition of enough magnesia to an appropriate mixture of pure lime and silica will bring out the äkermannite. It is interesting to note in passing that magnesia in mixtures of tricalcic silicate composition also develops the tricalcic silicate compound, but good crystals are not obtained by using oxide of iron, vanadic acid or other usual laboratory fluxes.

Of the pure silica, six different crystalline forms with definite regions of stability were described in the earlier work, and one of lime, but with the important corollary, in the case of the latter, that the properties of the so-called amorphous (burned) lime differ

in some important particulars from the more coarsely crystallized form. Two crystalline forms of calcium metasilicate were established and designated α (sometimes called pseudowollastonite), and β (corresponding to the natural mineral wollastonite). Three stable crystalline forms of the orthosilicate with definite properties were established, defined and given the names α -, β -, and γ -orthosilicate, the α -form being

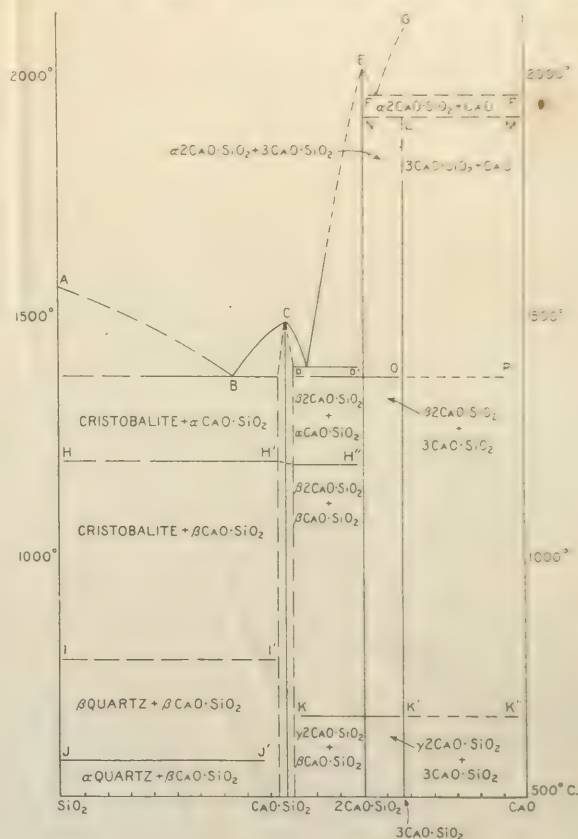


Fig. 1.

the first crystalline form to appear in the melt. In addition to these, a fourth and apparently unstable crystalline modification has now been discovered, which may be of importance in the constitution of Portland cement. To avoid confusion, the new modification has been designated β' . The new compound, tricalcic silicate, has so far been found in but a single stable crystalline form.

These compounds when brought together in varying compositions yield eutectics as follows: (1) At 37 per cent. lime, between pure silica and the metasilicate; (2) at 54 per cent. lime, between the metasilicate and orthosilicate; (3) 67.5 per cent. lime, between the orthosilicate and pure lime. The tricalcic silicate becomes unstable in the vicinity of 1900° C. and does not appear to enter or come out of the binary melt as such. For this reason it does not enter into eutectic or other relations with the adjacent compounds, calcium orthosilicate and lime. Since Fig. 5 was drawn, a small field has been discovered in which there

¹ "The Lime-Silica Series of Minerals," Arthur L. Day, E. S. Shepherd and F. E. Wright, *Am. J. Sci.*, [4] **22**, 265 (1906). "The Binary Systems of Alumina with Silica, Lime and Magnesia," E. S. Shepherd, G. A. Rankin and F. E. Wright, *Ibid.*, [4] **23**, 293 (1909).

² J. H. L. Vogt, *Die Silikatschmelzlösungen*, II, **22**.

is a crystal similar to äkermannite but of a composition, $3\text{CaO} \cdot 2\text{SiO}_2$. The relation of this phase to the binary system is quite similar to that of the tricalcic silicate.

The melting temperatures of the compounds and eutectics are all relatively high. Pure silica melts to a liquid of extreme viscosity at about 1600° , the eutectic between silica and calcium metasilicate melts at 1426° , the metasilicate itself (α -form) at 1540° , the eutectic between the α -metasilicate and the α -orthosilicate at 1440° , α -orthosilicate at 2086° , and, finally, the eutectic between α -orthosilicate and pure lime at 2015° . The melting point of pure lime is beyond the reach of accurate temperature measurement. The tricalcic silicate becomes unstable and dissociates into the orthosilicate and pure lime before the melting temperature is reached.

In entering upon the three-component diagram from the lime-silica side, we have to take account, therefore, of fifteen possible phases: Pure silica (six forms), calcium metasilicate (two forms), $3\text{CaO} \cdot 2\text{SiO}_2$ (one form), calcium orthosilicate (four forms), tricalcic silicate (one form), pure lime (one form). Many of these possible modifications are of minor significance for the study of the constitution of Portland cement.

Alumina-Silica Series (Fig. 2).—The alumina-silica series presents only one compound, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ —sillimanite—which forms eutectic mixtures with the pure components on either side of it. The eutectic between sillimanite and corundum occurs at 64 per cent. Al_2O_3 , temperature slightly below the melting

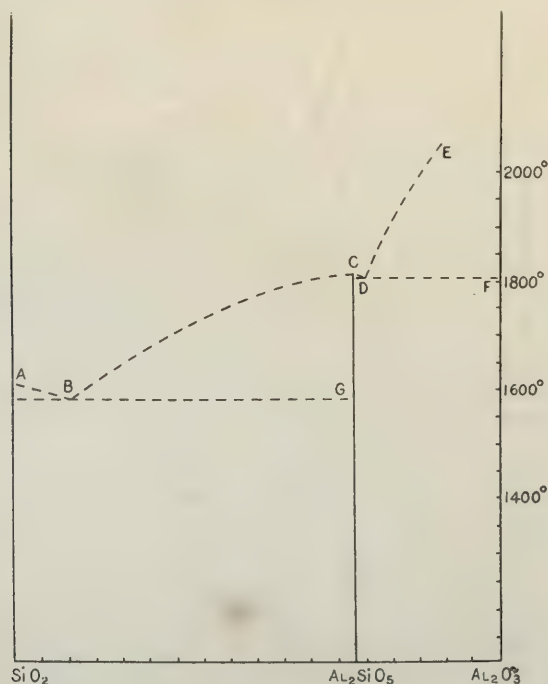


Fig. 2.

point of pure sillimanite (1816°). The eutectic between sillimanite and cristobalite also occurs just below 1600° . Two other crystal forms of $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (andalusite and cyanite) occur in nature, but they have neither been successfully formed in the laboratory nor has their relation to sillimanite been satisfactorily

established beyond the fact that they go over into sillimanite on heating.

Entering the triangular diagram from this side, there is, therefore, but one stable phase which may be expected to participate in addition to the pure components, alumina and silica.

Lime-Alumina Series (Fig. 3).—This series was found to contain four compounds in addition to the

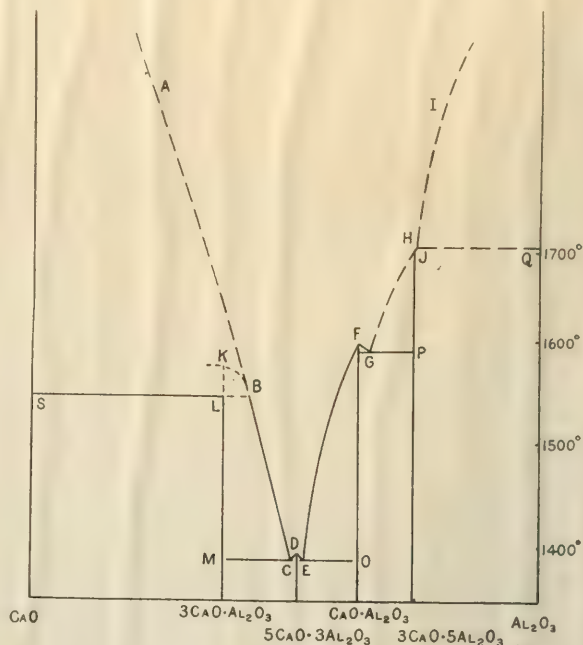


Fig. 3.

original components, and three eutectics. The compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is unstable at its melting point, in consequence of which the invariant system CaO , $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, liquid and vapor, does not reach a minimum temperature. The system $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$, Al_2O_3 , liquid and vapor, seems to present a similar case, though the temperature is too high to make this determination certain. There is a monotropic form of both the $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$. $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ present normal maxima.

Entering the three-component diagram from the lime-alumina side, four stable phases may therefore be expected to participate. The two unstable forms thus far discovered do not appear with any regularity in any of the three-component mixtures studied.

New Phases.—Before entering upon the detailed discussion of the three-component system, it remains to describe the new two-component phases which have been discovered since the publication of the earlier papers referred to. Of these two, the tricalcic silicate and the β' form of the orthosilicate, may be important constituents of Portland cement. Of these, the β' form of the orthosilicate is wholly new, but the tricalcic silicate was sought for most diligently in the earlier study of mixtures of pure lime and silica, because of the very general opinion prevailing among students of cement problems that this compound existed and formed one of the most important components of Portland cement; but no trace of it was

ever found. The examination of the mixtures of this composition made with great care in this laboratory, together with some preparations made by such distinguished experts as Newberry and Richardson, yielded one of the forms of the orthosilicate and an excess of free lime in every instance. The invariable reappearance of mixtures of orthosilicate and free lime in preparations of tricalcic silicate composition, in place of the homogeneous product necessary to define and establish the properties of a new compound, when combined with the equally persistent reappearance of the orthosilicate inversion at 1410° throughout the region where the tricalcic silicate should appear if such a compound existed, and the complete absence in a very extensive literature of any adequate evidence of homogeneity in the products to which the name *tricalcic silicate* has been given, led us to the positive conclusion that no compound of tricalcic silicate composition existed. All this evidence still remains unshaken, and yet the compound tricalcic silicate has recently been prepared in a state of high purity and homogeneous, except for a persistent trace of the orthosilicate, or lime, or both, which varies in amount from one to two per cent. in individual cases. This somewhat contradictory situation requires the addition of but a single experimental observation to clear it up completely: the tricalcic silicate has been found to be unstable at its melting temperature and for some distance below, so that a melt of this composition invariably crystallizes on cooling to orthosilicate and lime, which then appear with the properties and in the successive modifications already described. In the presence of alumina or even alone, if held for a sufficient time at temperatures in the vicinity of 1800° , the orthosilicate and lime combine to form a new compound with new and independent properties and homogeneous within the limits above noted.

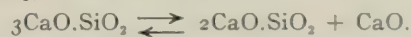
The new compound has an index of refraction practically identical with β -orthosilicate, but in the binary system we have never been able to develop crystals of it which were large enough to allow a satisfactory determination of its optical character. In the ternary system, fair-sized crystals have been obtained and prove to be weakly birefracting and *optically negative*. The relations in the binary system were further complicated by the discovery of the apparently instable β' form of the orthosilicate which is also weakly birefracting, but optically positive.

After a long search for the composition of this new optically negative phase, we were able to assure ourselves, by means of a large number of preparations varying in composition by one per cent. and often by only half of one per cent., that preparations approaching $3\text{CaO} \cdot \text{SiO}_2$ were richer in this new phase. This seemed to point definitely to the existence of a new compound in the binary series, but the 3 : 1 and 4 : 1 mixtures of the pure components when fused in the iridium furnace (2000° – 2100° C.) gave only well crystallized *lime* and *orthosilicate*, as before. Preparations made from very finely ground lime and silica, or even from precipitated (gelatinous)

silica and hydrated lime, did not yield a homogeneous preparation with good optical properties.

We had already observed that the ternary preparations, after being heated in the gas furnace, or baked (without melting) for days or weeks in the platinum furnace at temperatures near 1500° , gave large amounts of this optically negative phase. But the same preparation when *melted* in the iridium furnace gave large quantities of lime and orthosilicate and much less of the optically negative material. It was here that we began to suspect that the optically negative phase was instable in contact with the melt.

We then tried combining lime and silica in the 3 : 1 ratio by baking them for a long time in the platinum furnace. But even so we were unable to obtain crystals whose optical character could be satisfactorily determined. Subsequently, the preparations were baked for several hours in the iridium furnace at about 1800 – 1900° C. By this means we were able to obtain a *nearly* homogeneous material which upon fusion went over into lime and orthosilicate but of which again the optical character could not be definitely ascertained. The 74.5 per cent. CaO preparation had always lime in excess, while the 72.5 per cent. preparation contained orthosilicate in excess. On the other hand, the presence of 0.5 per cent. Al_2O_3 proved to be quite sufficient to develop the crystals, but the preparation is not homogeneous. Finally, mixtures of the 3 : 1 composition were baked until they were practically homogeneous and consisted of the weakly birefracting material. Then they were fused and allowed to recrystallize, whereupon they yielded products in which only CaO and $2\text{CaO} \cdot \text{SiO}_2$ could be discovered. The reaction is evidently somewhat slow especially before the appearance of the liquid phase. It is not impossible, therefore, that we have placed the dissociation temperature a little too high. As the result of all the observations (some 800 in number), one may conclude that $3\text{CaO} \cdot \text{SiO}_2$ belongs to that class of compounds which form by reaction between the solid components, but which decompose before the melting temperature is reached, *i. e.*, they are wholly unstable in contact with the melt. This relation is indicated by the line NLM in figure 1, ($3\text{CaO} \cdot \text{SiO}_2 + \text{CaO} + \text{Ca}_2\text{SiO}_4$). L is the quadruple point at which $3\text{CaO} \cdot \text{SiO}_2$ decomposes to form lime and Ca_2SiO_4 ; thus



The reaction is reversible though it may be expected to proceed slowly by reason of the phases being solid and vapor. The time factor becomes a serious consideration once the preparation has been melted and allowed to crystallize again into lime and orthosilicate crystals of relatively large dimensions. These will combine to form tricalcic silicate under favorable conditions but with extreme slowness. In the ternary system the liquid phase appears a little above 1400° C. and greatly facilitates the reaction. It is a noticeable fact that while certain ternary concentrations containing several per cent. of Al_2O_3 when suddenly cooled from 1600° C. show a certain quantity of free lime, the same preparations show a much

greater quantity when cooled from 1750° . On being reheated at 1600° the quantity of lime diminishes, showing a ready reversibility, *i. e.*, the concentration of the melt follows along the boundary curve just as would be expected.

If this phase were merely instable at its melting point like the tricalcic aluminate, then after fusion, one might expect a mixture of CaO , $3\text{CaO} \cdot \text{SiO}_2$ and Ca_2SiO_4 , but lime and orthosilicate only are found, so that the evidence is all in support of the view that tricalcic silicate in the binary series is never stable in contact with the melt. The observations in the ternary system lead to the same conclusion. The binary diagram (Fig. 1) therefore has the new lines N-L-M $3\text{CaO} \cdot \text{SiO}_2$ added and the dotted lines O P and K' K'', which indicate that the inversions $\alpha \rightleftharpoons \beta$ and $\beta \rightleftharpoons \gamma$ in the orthosilicate are instable extensions of these inversions into the field belonging to $3\text{CaO} \cdot \text{SiO}_2 + \text{CaO}$.

A New Form of Ca_2SiO_4 .—An old and hydrated sample of orthosilicate when quickly cooled from a temperature of 1425° yielded a weakly birefracting and optically positive crystal which could not be obtained with fresh preparations. Attempts to locate the inversion temperature by thermal means showed two heat changes about 30° apart, one of which disappeared after a few heatings and could not again be obtained. Except for water and probably some carbon dioxide, the preparation was pure. We regard this form as instable. It appears occasionally in the ternary mixtures, but with no regularity.

In brief résumé then, we find in the binary series between pure lime and pure silica four compounds:

CaOSiO_2 —two forms α and β . M.P. $\alpha = 1540^{\circ}\text{C}$.

$3\text{CaO} \cdot 2\text{SiO}_2$ —one form.

$2\text{CaO} \cdot \text{SiO}_2$ —four forms, α , β , β' and γ of which β' is monotropic.

$3\text{CaO} \cdot \text{SiO}_3$ —instable in contact with the melt, the quadruple point falling at about 1900°C .

There are three eutectics:

$\alpha\text{CaO} \cdot \text{SiO}_2 + \text{SiO}_2$ 1426°C .

$\alpha\text{CaO} \cdot \text{SiO}_2 + \alpha_2\text{CaO} \cdot \text{SiO}_2$ 1440°C .

$\alpha_2\text{CaO} \cdot \text{SiO}_2 + \text{CaO}$ 2015°C .

The inversion $\alpha\text{CaO} \cdot \text{SiO}_2 \rightleftharpoons \beta\text{CaO} \cdot \text{SiO}_2$ occurs at about 1102°C .

The inversion $\alpha_2\text{CaO} \cdot \text{SiO}_2 \rightleftharpoons \beta_2\text{CaO} \cdot \text{SiO}_2$ occurs at about 1410°C .

The inversion $\beta_2\text{CaO} \cdot \text{SiO}_2 \rightleftharpoons \gamma_2\text{CaO} \cdot \text{SiO}_2$ occurs at about 675°C .

It will be recalled that this last inversion is accompanied by a 10 per cent. volume change which causes the "dusting" of the orthosilicate and preparations containing it in considerable quantity. In our experience, however, the absence of "dusting" does not prove that orthosilicate is not present in a considerable quantity.

The Ternary System, $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$.—The nature of the binary systems having been cleared up, we are now in a position to make a systematic examination of the ternary system. While one cannot predict from the nature of the binary series, just what will be the ternary relations, it is of advantage to know

that binary compounds may occur as stable phases within the diagram.

In Fig. 4 the results of the binary studies are projected upon the sides of the ternary diagram. Since the compositions $\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ are at maximum temperatures with eutectics at A, B, C, E, F, G, I and J, boundary curves limiting the fields for the stable

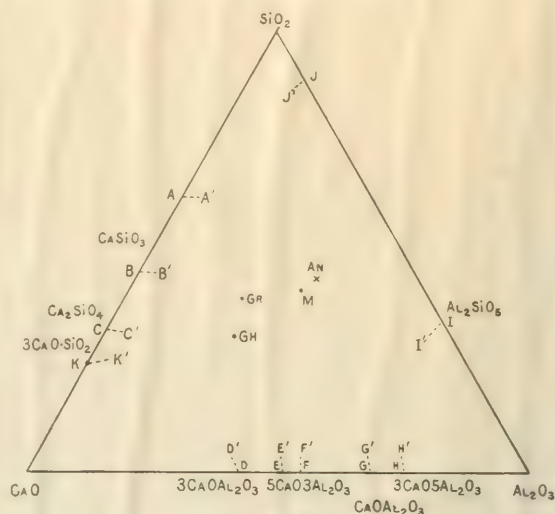


Fig. 4.

existence of the compounds (monovariant systems) will extend out into the diagram at AA', BB', CC', EE', FF', GG', II' and JJ'. Similarly, monovariant systems beginning at D, H and K will be found on the lines DD', HH' and KK'. Nothing definite as to the course of these boundary curves can be predicted from the binary systems.

We also find among the natural minerals the ternary compounds anorthite (An), Meionite (Mi), Gehlenite (Gh) and Grossularite (Gr), all lime-silica-alumina minerals. Of these, pure grossularite decomposes on melting into a mixture of anorthite with (probably) gehlenite (?) and pseudo-wollastonite, and does not appear on the fusion surface of the ternary system. We have prepared it by the reaction of AlCl_3 on Ca_2SiO_4 in water under pressure. Meionite does not form by fusing together the pure oxides, but a crystal similar to gehlenite occurs, and must be included in the equilibrium diagram.

We may, therefore, anticipate the appearance of at least two fields for ternary compounds and ten fields for the binary compounds belonging to this ternary system. Wollastonite becomes stable over a small region of the ternary diagram where the fusion surface for CaSiO_3 falls below the inversion temperature of this compound. The β -orthosilicate of calcium may also have a small field of stability depending on the slope of the orthosilicate fusion surface.

After this general reconnaissance of the field, it may be studied in detail experimentally. For research of this kind there are three general methods of attack.

1. One may make up the ternary mixtures observing the usual precautions¹ and then from the

¹ See "Binary Systems," *etc.*, *loc. cit.*, p. 206.

energy changes in the system which are registered by the thermoelement, endeavor to unravel the phase relations. This method is invaluable, but like all methods employed in the exploration of new fields, it gains strength when employed in conjunction with other methods even though the latter be inferior in the scope of their practical application. With silicates as with alloys, it is much easier to interpret the thermal data if one knows the nature of the reacting phases.

2. The second method is to bake the different preparations for long periods of time at appropriate

is usually done, either by adding the phase under investigation and finding out whether or not it dissolves in the saturated solution or the saturated solution is allowed to crystallize slightly in order that the first crystals to form may be identified.¹ The latter method best serves our purpose here. A small amount of material of the desired composition is placed in a furnace and held at constant temperature until on quenching (sudden cooling by dropping into a bath of mercury or water), only one kind of crystal is present, and the rest of the solution is cooled to glass before it has time to crystallize. The

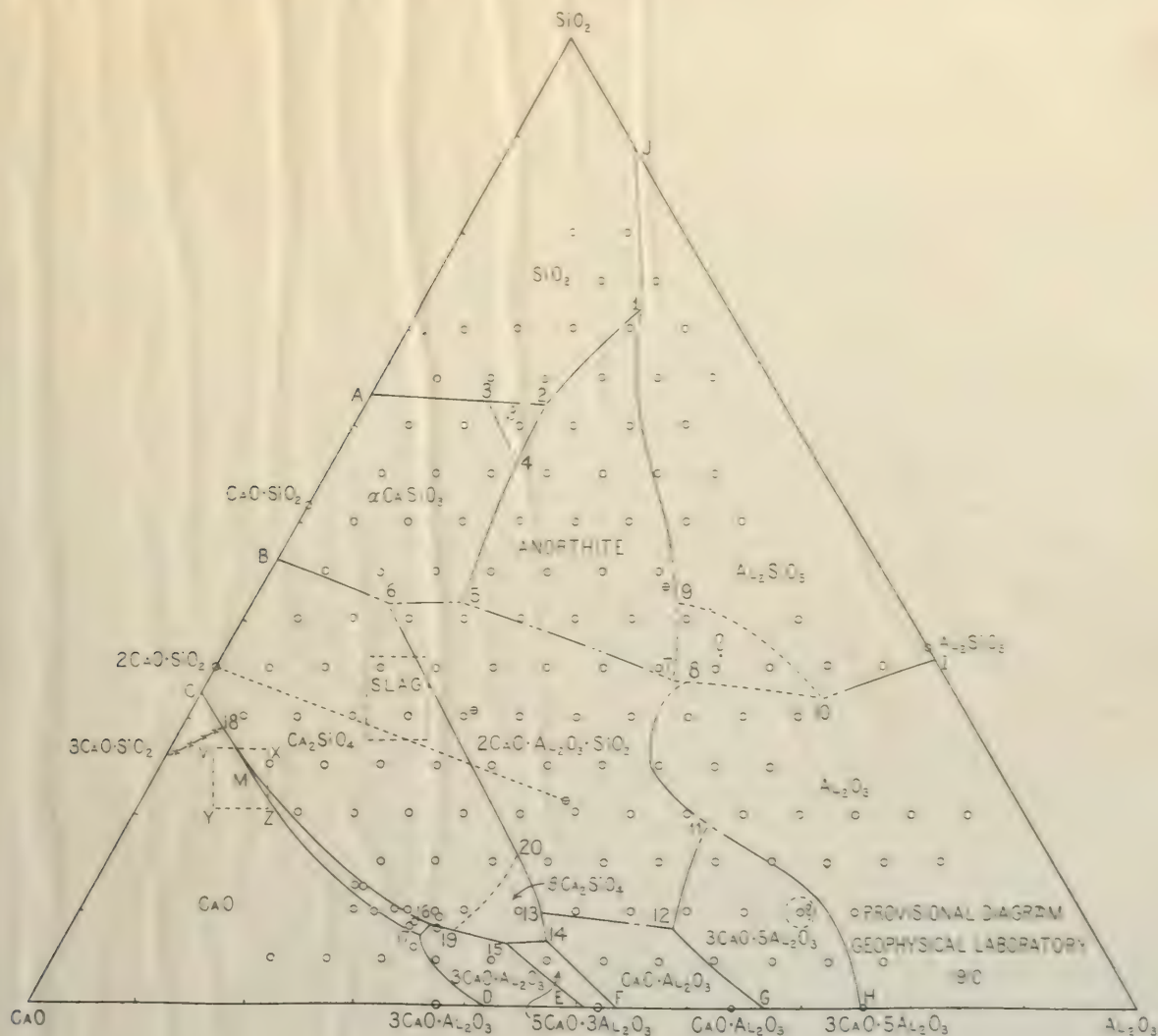


FIG. 5

temperatures in order to allow time for the reactions to become complete, and the crystals to grow to measurable size, which renders microscopic examination much easier. With these two methods together, we have covered the major portion of the lime-silica-alumina diagram.

3. The third method has for its object the determination of the boundaries of the various fields in which particular phases have their stable existence, *i. e.*, of the location of the boundary curves. In the case of ternary systems at ordinary temperatures, this

exact temperature for any given mixture must be determined by a series of trials with sufficient variation of the conditions of experiment to rule out hysteresis effects. Temperatures will thus be found where the charge is wholly glass, and also where the product obtained by quenching is wholly crystalline. The method also allows the crystals time to grow to measurable size, thus assisting the microscopic identification. In other words, the method develops the primary phase (Bodenkörper) embedded in the glass

¹ Cf. Roozeboom.

(solution) and allows a rapid and very satisfactory mapping of the fields of stability for each phase. The method fails when the temperature rises too high for the platinum furnace (1600°). The iridium furnace (1600° – 2100°) does not serve well for this method. Naturally, the method does not work so well where two kinds of crystals are present. To get the most satisfactory results, *i. e.*, fair-sized crystals of the primary phase, the charge should be held at a temperature just below that of complete fusion for the composition in question.

In this way, the limits of the various fields were found as indicated in Fig. 5. The dots given in the diagram do not indicate all of the concentrations examined nor the many heat treatments and examinations required to determine the relations of any one concentration. The entire ternary system thus far has necessitated the preparation of about five hundred different concentrations and fully five thousand heat treatments and microscopic examinations. While the location of the fields and boundary curves is now fixed within $\pm 2\frac{1}{2}$ per cent., the *exact location of the ternary eutectics and other quintuple points* other than points 13, 14, 15, 16 and 17, which are now determined, *remains to be established by later work*. They have been located in this diagram by following the general slope of the boundary curves, and by applying the theorem of van Rijn van Alkemade¹ wherever practicable.

The phase $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (first observed by Boudouard) is very similar in optical properties to the mineral gehlenite, but its composition is quite different. This phase appears at a maximum temperature in the fusion surface and is the pure type for this ternary system. Mixtures of the composition of typical gehlenite do not show a maximum temperature nor are they ever homogeneous. They also show thermal changes corresponding to the boundary curves.

The diagram here given is one of moderate complexity, but the crystallization curves for any given composition follow the general laws for such curves, set forth by Geer² in his paper on crystallization in three-component systems.

From this diagram, it appears that cement clinker, *i. e.*, clinker whose essential composition falls approximately within the area xyz , should consist chiefly of $3\text{CaO} \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$ with a small amount of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. With the exception of the small corner lying below the broken line connecting $3\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (Fig. 10), all compositions within the field xyz freeze solid at point 16. Those lying within that corner of the rectangle xyz will freeze solid at point 17 and contain free lime.

Let us next consider the results obtained by prolonged annealing of these various mixtures at high temperatures.

Carefully prepared and thoroughly combined charges

were enclosed in small platinum cups which were placed in the platinum furnace and heated for periods of from two to three weeks at temperatures ranging from 1300° – 1500°C ., the temperature depending on the composition of the charge. After this treatment, the material was examined with the microscope and

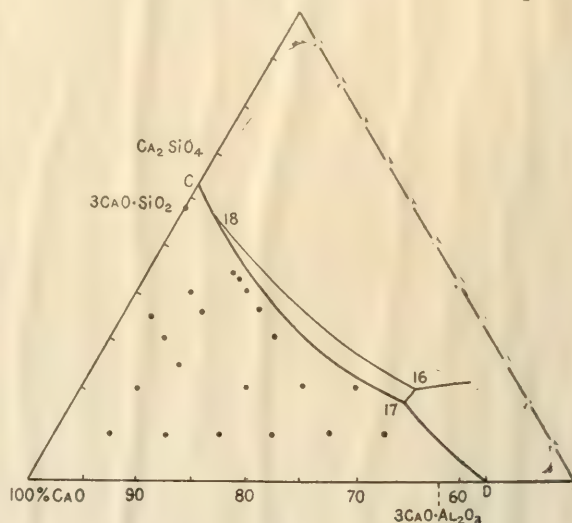


Fig. 6.

the different compounds identified. Crystallized CaO (free lime) was positively identified in all of the compositions indicated by dots in Fig. 6. This does not mean (as in Fig. 5) that CaO was the only solid phase present, but that it was one of the phases present. From the general theory, free lime should not occur to the right of the line joining the compositions $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{SiO}_2$, and this is found to be approximately true.

In Fig. 7 are shown some of the compositions in which orthosilicate is present. The small amounts

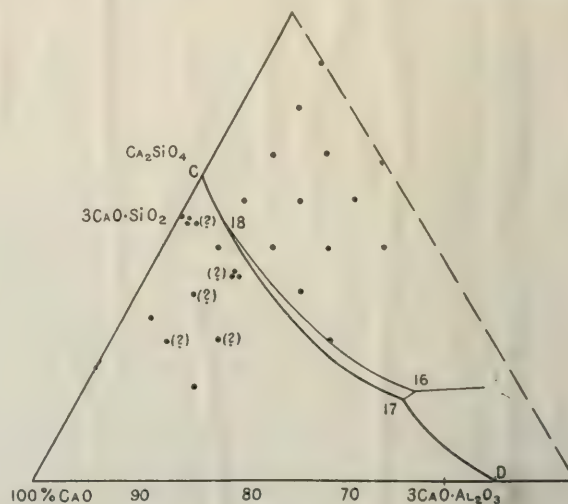


Fig. 7.

of orthosilicate which still exist in samples below the boundary curve 18–17 can only mean that equilibrium has not become fully established. Even where a large excess of lime is present, the orthosilicate does not always completely change to tricalcium silicate.

¹ A. C. van Rijn van Alkemade, *Z. phys. Chem.*, **11**, 289 (1893).

² "Crystallization in Three-Component Systems," W. C. Geer, *J. Phys. Chem.*, **8**, 257 (1904). This is a very important paper for those who wish to study the relations existing in such a system as this. As Geer's deductions have not yet found their way into the text books, we venture to call particular attention to the paper.

$3\text{CaO} \cdot \text{SiO}_2$ in the Ternary System.—In Fig. 8 a small section (the triangle CaO 65 per cent., SiO_2 35 per cent.; CaO 80 per cent., SiO_2 20 per cent.; and CaO 65 per cent., Al_2O_3 15 per cent., SiO_2 20 per cent.) of the ternary diagram is plotted on a much larger scale. The dots indicate some of the concentrations in which the

16 and 17, compositions which showed $3\text{CaO} \cdot \text{SiO}_2$ as the primary phase were obtained.

It is desirable to know the exact direction which these boundary curves take and the exact location of quintuple point 18. This cannot yet be done with precision, but from theoretical considerations, point 18 should fall at or very near to the temperature corresponding to the point L in the binary system, *i. e.*, about $1900^\circ \text{C}.$, and quenchings from the iridium furnace indicate that the path given is about right. From the lower portion of the fields where we have been able to locate the boundary curves definitely, and from the general slope of the surfaces, it seems probable that the field for tricalcic silicate will be approximately that which has been assigned to it. It may prove to be slightly broader at the higher temperatures, but experimental evidence of this is at present very difficult to obtain, and the indications above mentioned do not support this view. As far as the cement problem is concerned, the practical results will be unaffected either by shifting the location of point 18 or broadening the upper part of the field for $3\text{CaO} \cdot \text{SiO}_2$.

In Fig. 9, the dots indicate the compositions in which $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ occurs as one of the phases. A circle instead of a dot indicates that the identification was not absolute but is highly probable. The crystals in such cases were too small for positive identification but such optical properties as could be determined

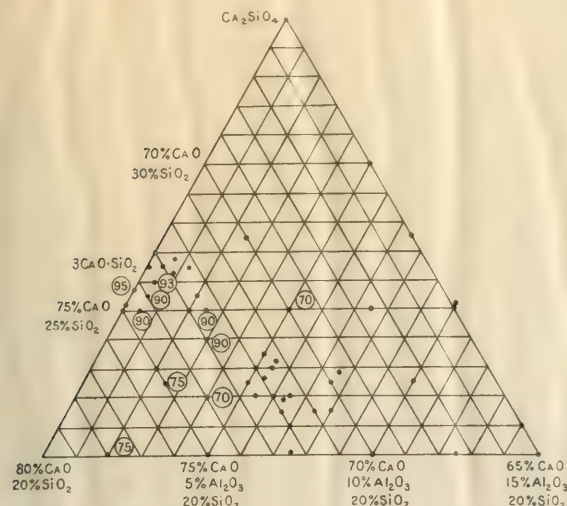


Fig. 8

optically negative crystals with low birefringence (tricalcic silicate) occur. The numbers enclosed in circles represent the approximate percentage of this phase, in the charge examined. Thus ninety means that under the microscope this composition appeared to consist of about 90 per cent. $3\text{CaO} \cdot \text{SiO}_2$ and varying amounts of orthosilicate or lime. The estimate is merely approximate. It will be noticed that while at 0.5 per cent. Al_2O_3 the tricalcic silicate amounts to 90–95 per cent. or more of the total charge, at 5 per cent. Al_2O_3 it has fallen to about 70 per cent. In the binary series a change of 1 per cent. in the concentration on either side of $3\text{CaO} \cdot \text{SiO}_2$ gave a small excess of lime or of orthosilicate, while the body of the charge consisted of the weakly birefracting, optically negative phase. We may, therefore, regard the $3\text{CaO} \cdot \text{SiO}_2$ as a definite compound, although we have not yet been able to obtain it entirely free from pure lime, orthosilicate, or in well crystallized units. In fact, observations of its optical character with the microscope become increasingly difficult as the composition approaches to homogeneity by reason of the extremely fine-grained and closely interwoven character of the crystalline mass. This situation, by the way, has frequently been encountered before, both in our own work and in the literature of similar studies at low temperatures, the purer the substance the more difficult it often becomes to secure well developed individual crystals of it. We have no evidence that tricalcic silicate forms solid solutions with alumina, lime or orthosilicate, nor is any solid solution formed with ferric oxide.

With the present equipment it has not yet proved possible to determine the exact course of the boundary curves 18–16, 18–17, but in the lower portion of this field, *i. e.*, in the neighborhood of the quintuple points

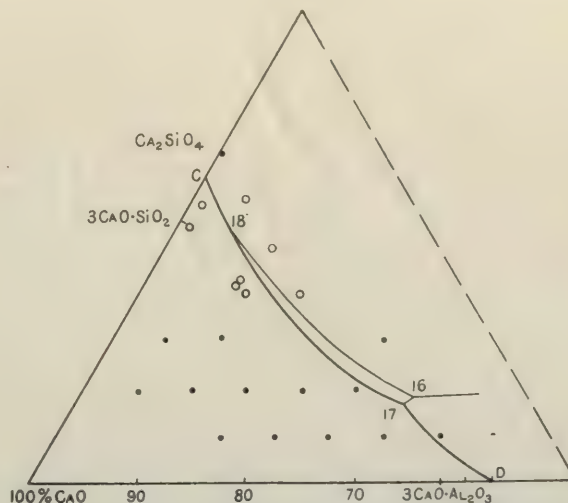


Fig. 9.

agree with the properties of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. As this phase is present in very small amount as a part of the eutectic residue, it is naturally fine-grained and difficult to identify positively, but with two of the three probable phases positively identified, a high degree of probability attaches to the indications of the third.

GENERAL OBSERVATIONS ON THE TERNARY SYSTEM.

Crystallization Curves for Cement Clinker.—If a charge of the composition 8.5 per cent. Al_2O_3 , 68.6 per cent. CaO and 22.9 per cent. SiO_2 (Point M., Fig. 10) be completely fused and then allowed to freeze normally, *i. e.*, without undercooling, the following changes

occur: Over the range from M, where the first crystals appear, CaO will crystallize out until the composition of the melt reaches the boundary curve at N. At this point, $3\text{CaO} \cdot \text{SiO}_2$ begins to separate and the concentration of the melt begins to follow the boundary curve, both CaO and $3\text{CaO} \cdot \text{SiO}_2$ separating. From the slope of the boundary curve as here drawn it follows that the lime which has separated will be used up to form $3\text{CaO} \cdot \text{SiO}_2$, after which the crystallization curve will promptly cross the field for $3\text{CaO} \cdot \text{SiO}_2$ and follow down boundary curve 18-16 growing solid at point 16 to a mixture of $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$ and

dissolved the orthosilicate will begin to separate following curve 18-16. Concentrations lying in the upper right-hand corner of $vxyz$ —above the curve 18-16—will have $2\text{CaO} \cdot \text{SiO}_2$ as primary phase, as in the case of the neighboring composition T, for example. When the composition T begins to freeze, $2\text{CaO} \cdot \text{SiO}_2$ separates as the primary phase and continues to do so until the boundary curve is reached at U. From U to 16, both $3\text{CaO} \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{SiO}_2$ separate, the charge solidifying at 16, to a mixture of $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Between the boundary curves 18-16 and 18-17, $3\text{CaO} \cdot \text{SiO}_2$ would

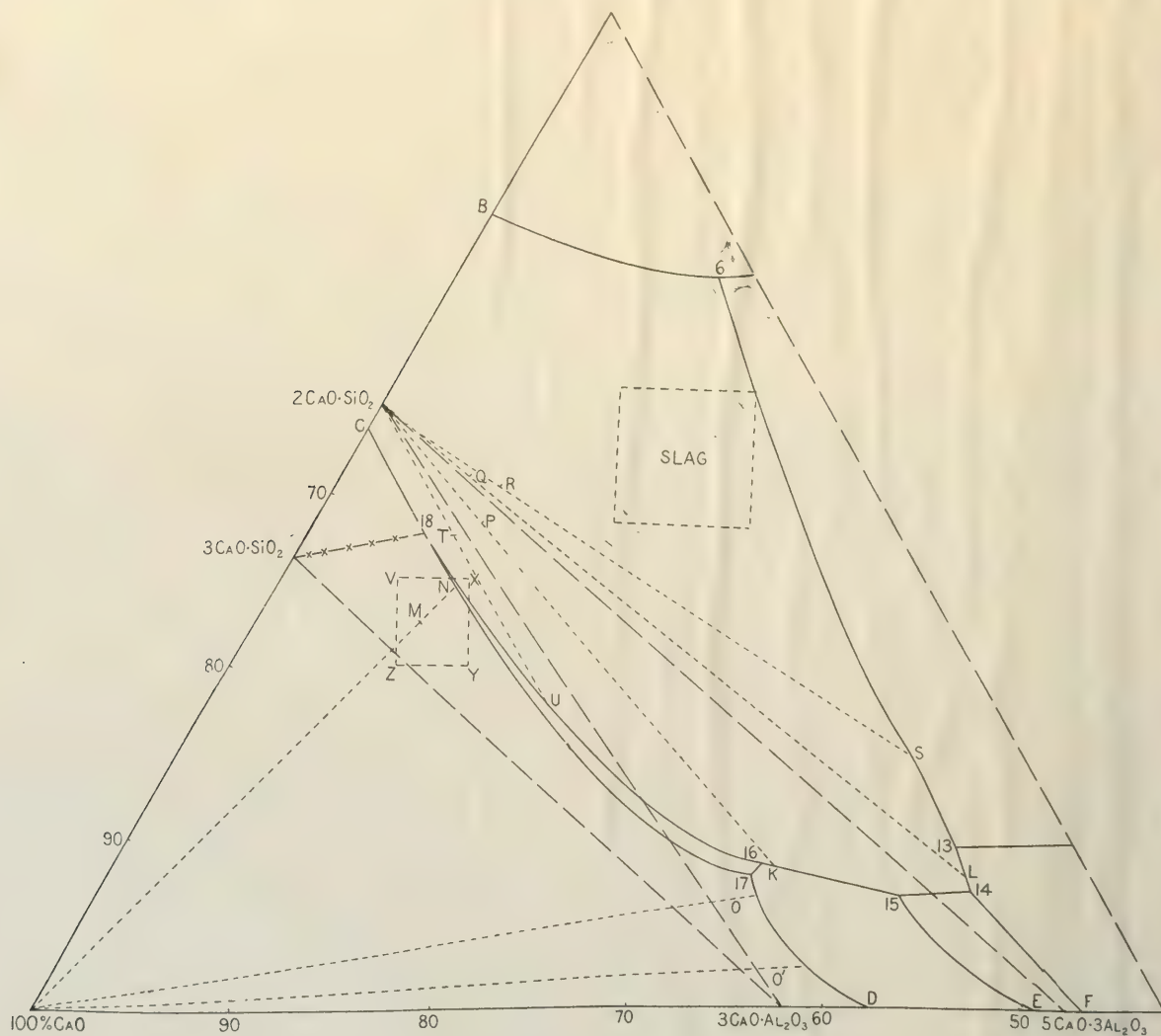


Fig. 10.

$3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Compositions can be taken for which the crystallization curve will follow 18-17 without crossing the field for $3\text{CaO} \cdot \text{SiO}_2$, but such compositions will probably not enter into the problem of cement clinker. On remelting, the changes will occur in the reverse order. Thus in any cement of a composition lying within the field $vxyz$, below the boundary curve 18-17, and above the broken line joining $3\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, free crystalline CaO will first separate and as crystallization proceeds, be redissolved to form tricalcic silicate. After the excess of CaO has been

be the primary phase but would be quickly joined by $2\text{CaO} \cdot \text{SiO}_2$.

In other words, all compositions lying within the triangle formed by joining $3\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ will freeze solid at point 16 to a mixture of these three phases.

All concentrations (as, for example, z) lying within the triangle CaO, $3\text{CaO} \cdot \text{SiO}_2$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ would freeze solid at point 17, to a mixture of lime, tricalcic silicate and tricalcic aluminate. The change in the concentration of CaO in molten mixtures of Portland

cement composition inside the rectangle $vx y z$ varies but little along the first branch of the crystallization curve. The relation of the cement concentrations is such that very little of the primary phase separates and practically the whole charge crystallizes as secondary and tertiary crystals. In other words, the conditions are the most favorable possible for small crystals, and so-called eutectic structure. Furthermore, it will be remembered that it is characteristic of $2\text{CaO} \cdot \text{SiO}_2$ to form in very small, closely intergrown crystalline masses with intricate twinning. In practice one cannot predict the phases which will be the first to form in a mixture of the pure oxides of composition M when heated, but as soon as the temperature rises high enough, the combination will progress toward the grouping represented by point 16, thence the general trend will be the reverse of the above mentioned crystallization curve to N, etc. If the charge is not finely ground and intimately mixed, the reaction will not have the opportunity to go forward promptly and a poor product containing an excess of uncombined lime results. Similarly, if the temperature is too low an excess of uncombined, so-called amorphous lime (*i. e.*, of very fine-grained lime crystals) results.

All concentrations within the triangle $3\text{CaO} \cdot \text{Al}_2\text{O}_3 - 2\text{CaO} \cdot \text{SiO}_2 - 5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (as, for example composition P, Fig. 10) will solidify at quintuple point 15 to a mixture of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, $2\text{CaO} \cdot \text{SiO}_2$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$.

A most interesting case occurs in this field to which the attention of petrologists should be especially directed. It exhibits the important case of a stable phase crystallizing from a cooling magma only to be completely resorbed at a lower temperature. All this occurs without interruption of the normal cooling or the introduction of any disturbing factor from without. The lime crystals first formed from the composition represented by O for example are redissolved at the boundary curve 17-D to form $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, the last of the free lime disappearing at the quintuple point 17. In systems of more than three components, which includes all rocks, this phenomenon of resorption will probably occur more frequently than in simple three-component systems. It is also to be noted that along any of these boundary curves, two kinds of crystals are separating side by side, a condition which is sometimes spoken of as producing and being characteristic of *eutectic structure*. Of course such a characterization has significance only when it occurs in a two-component system. In polycomponent systems, such a structure—even if it were proved to be characteristic, which for rocks is still uncertain—would not necessarily define eutectic composition.

In passing, it may be noted that the crystallization curve of the composition O' will not proceed to quintuple point 17 but will leave the boundary curve D-17 and cross the field for $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, striking boundary curve 16-15 and solidifying at point 15. Similarly, from the composition indicated by R $2\text{CaO} \cdot \text{SiO}_2$ would separate as primary crystals, after which the crystallization curve would meet the boundary curve between $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and orthosilicate

at S and the charge would probably solidify at 13 to a mixture of orthosilicate, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$.

From theoretical considerations, points 13 and 14 should not have the relation to each other which is indicated in this diagram without an additional phase in the neighborhood of point 13, which a very careful search has so far failed to develop with sufficient certainty for its identification.

The field included within the quintuple points 8, 9 and 10 also belongs to a crystal whose composition is not yet determined, and a strange phase occurs at CaO 25 per cent., Al_2O_3 15 per cent. and SiO_2 10 per cent., which has not yet been identified.

Those boundary curves which show an apparent double curvature will doubtless find explanation after a further study of the curves and the adjacent stable phases.

To what extent the different forms of calcium orthosilicate differ in their cement-forming properties also remains to be investigated. Neither is it known to what extent the relations here presented will be affected by the impurities of the industrial clinker. It is highly improbable that they will be altered in any fundamental manner, but it might prove imprudent to apply the above examples of crystallization curves to a system containing other components until the influence of such components has been definitely established, just as it is now shown to have been shortsighted to assume that there could be no tricalcic silicate because it did not form in mixtures of pure lime with pure silica.

From the information which has been gathered already it is plain that the final product of crystallization will be greatly influenced by relatively small differences in the amount of lime in the clinker. Approximately 5 per cent. difference in the CaO content includes all five of the possibilities represented by the crystallization curves of Z, M, P, T and R. It may also appear that the field $vx y z$ is too high in its lime concentration. We have so far made no experiments to prove that the area $vx y z$ includes the compositions which give the best pure cement clinker. It was placed there following Richardson's data.¹ It is also commonly assumed that MgO and Fe_2O_3 replace CaO and Al_2O_3 respectively, but we have no data at present upon the validity of this assumption.

After the equilibrium conditions have been approximately established, it becomes a relatively simple matter to make up cement clinker which will contain free lime (concentrations within the triangle $\text{CaO} - 3\text{CaO} \cdot \text{SiO}_2 - 3\text{CaO} \cdot \text{Al}_2\text{O}_3$), and clinker which will not contain free lime (concentrations lying inside the triangle $3\text{CaO} \cdot \text{Al}_2\text{O}_3 - 3\text{CaO} \cdot \text{SiO}_2 - 2\text{CaO} \cdot \text{SiO}_2$), in both of which cases the alumina is present all or in part as $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. Or one can prepare clinker similar to composition R where the compounds present will be $2\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$,² and $\text{CaO} \cdot \text{Al}_2\text{O}_3$.

¹ "The Constitution of Portland Cement," Clifford Richardson, *Cement*, 5, 316 (1904).

² From the location of points 13 and 14 it seems possible that the phase $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ will finally disappear from concentrations outside of the triangle of which $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, Ca_2SiO_4 and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ are the apices, leaving Ca_2SiO_4 , $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$ as the final product.

with no $3\text{CaO} \cdot \text{Al}_2\text{O}_3$; or like P, whose final crystallization gives mixtures of $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. From such clinkers it should be easy to decide just where the limiting concentrations lie from which the best cement clinker is obtained. In such experiments it will be *absolutely necessary* that sufficient time be allowed for establishing equilibrium. It will also be necessary to determine the rôle played by iron oxide and magnesia and their effect on the crystallization curves as above given.

In the case of slag cements if we assume them to have approximately the composition indicated by the dotted square in the diagram, the composition will be of the very highest importance. From the theorem of van Rijn van Alkemade, there should be a maximum in the boundary curve 6-13 (Fig. 5) at the point where the dotted line joining $2\text{CaO} \cdot \text{Al}_2\text{O}_3$, SiO_2 and $2\text{CaO} \cdot \text{SiO}_2$ cuts it. All compositions lying above this line will yield as the product of their final crystallization $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, calcium orthosilicate, and probably $3\text{CaO} \cdot 2\text{SiO}_2$, whereas concentrations lying below this line crystallize to $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, calcium orthosilicate and $\text{CaO} \cdot \text{Al}_2\text{O}_3$. The difference in the chemical nature of these two end-products ($3\text{CaO} \cdot 2\text{SiO}_2$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$) is very great, much greater than any changes brought about by similar concentration differences in the Portland cement region.

REVIEW OF EARLIER WORK.

While it is not desirable to attempt any extended review of previous investigations in a preliminary paper, it is important that a brief statement of the earlier work be presented.

The most important is of course LeChatelier's thesis on hydraulic cements.¹ In brief his conclusion

with the barium aluminates that $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ was the next definite combination of these oxides.

The Newberrys² also appear to have depended entirely upon whether or not the material was "volume constant" when treated with water, and concluded that cement clinker consisted of $3\text{CaO} \cdot \text{SiO}_2$ and $2\text{CaO} \cdot \text{Al}_2\text{O}_3$. This latter compound has eluded our most careful search and we are unable to believe in its existence. Of the two compounds whose individuality was inferred from the reaction with water, therefore, one proves to be real and the other not.

Subsequently, Richardson³ published the results of a long and painstaking study of the binary and ternary mixtures supposed to constitute Portland cement, his chief conclusion being that the clinker consists essentially of a solid solution of $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ in $3\text{CaO} \cdot \text{SiO}_2$. This conclusion is now admitted to be erroneous, and due to the inability of the older petrographic methods to disentangle these very fine-grained crystalline aggregates.

Boudouard⁴ sought to obtain a comprehensive view of the whole system of ternary and binary mixtures by fusion studies with Seger cones. For reasons already given in some detail,⁴ the methods which he used both for the identification of the essential compounds and the determinations of their temperatures of formation and stability are wholly untrustworthy and need not be discussed here.

The complete list of compounds of lime, silica and alumina which have been proposed by the above-mentioned investigators are contained in the table below, those supposed to be essential ingredients of Portland cement being printed in italics in each case:

TABLE I.

	LeChatelier.	Boudouard.	Newberry.	Richardson.	Geophysical Laboratory.
Calcium Silicates	$\text{CaO} \cdot \text{SiO}_2$ <i>$2\text{CaO} \cdot \text{SiO}_2$</i> <i>$3\text{CaO} \cdot \text{SiO}_2$</i>	$\text{CaO} \cdot \text{SiO}_2$ <i>$2\text{CaO} \cdot \text{SiO}_2$</i> <i>$3\text{CaO} \cdot \text{SiO}_2$</i> <i>$2\text{CaO} \cdot \text{SiO}_2$</i> <i>$3\text{CaO} \cdot \text{SiO}_2$</i>	$\text{CaO} \cdot \text{SiO}_2$ <i>$2\text{CaO} \cdot \text{SiO}_2$</i> <i>$3\text{CaO} \cdot \text{SiO}_2$</i>	$\text{CaO} \cdot \text{SiO}_2$ 2 forms <i>$2\text{CaO} \cdot \text{SiO}_2$</i> 4 forms. <i>$3\text{CaO} \cdot \text{SiO}_2$</i> dissociates before the melting temperature is reached.
Calcium Aluminates $\text{CaO} \cdot \text{Al}_2\text{O}_3$ <i>$(3\text{CaO} \cdot 2\text{Al}_2\text{O}_3)$</i> <i>$3\text{CaO} \cdot \text{Al}_2\text{O}_3$</i> $\text{CaO} \cdot \text{Al}_2\text{O}_3$ <i>$(2\text{CaO} \cdot \text{Al}_2\text{O}_3)$</i> <i>$3\text{CaO} \cdot \text{Al}_2\text{O}_3$</i> $\text{CaO} \cdot \text{Al}_2\text{O}_3$ <i>$(2\text{CaO} \cdot \text{Al}_2\text{O}_3)$</i> $\text{CaO} \cdot \text{Al}_2\text{O}_3$ <i>$3\text{CaO} \cdot \text{Al}_2\text{O}_3$</i>	$3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ + one unstable form. $\text{CaO} \cdot \text{Al}_2\text{O}_3$ $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ + one unstable form. <i>$3\text{CaO} \cdot \text{Al}_2\text{O}_3$</i> unstable at its melting point.

was that the clinker consists of $3\text{CaO} \cdot \text{SiO}_2$ (tricalcic silicate) and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (tricalcic aluminate). He was unable to prepare the $3\text{CaO} \cdot \text{SiO}_2$ by fusion of the oxides but believed that he had obtained it by decomposing a suitable mixture of the chlorosilicate, $\text{SiO}_2 \cdot 2\text{CaO} \cdot \text{CaCl}_2$, in steam. The product obtained in this way contained 1.2 per cent. of chlorine and could not be shown to be homogeneous for purposes of definition, nor could he obtain any of its properties other than its reaction with water—it was "volume constant," while the fused mixtures were not.

By fusion, he obtained several aluminates of which only the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is of interest here. This he found to be the *most fusible of the aluminates*. Although he did not obtain it pure, he inferred from analogy

The formulae enclosed in brackets have not appeared in our work thus far and seem to be wholly unsupported by experimental evidence. With the exception of Boudouard none of the earlier investigations attempted temperature measurements, nor were the relations between the different binary compounds determined. All of the investigators observed the "dusting" of the calcium orthosilicate and LeChatelier ascribed it properly to polymorphism. The dissociation of the tricalcic silicate could only be established after a furnace, capable of control at these very high temperatures had been developed. Similarly, the

¹ J. Soc. Chem. Ind., **16**, 887 (1897).

² Cement, **4**, 276, et seq. (1903).

³ Rev. d. Metal., **1905**, 462.

⁴ Am. Journ. Sci., (4), **22**, 268 (1906).

¹ Annales des Mines, **1887**, 345.

dissociation of the $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ is very important in its effects on the reactions in the ternary system.

In none of the earlier studies had sufficient stress been laid upon the fact that in a ternary system the final product will, except in very special cases, always consist of at least three solid phases. Whether or not these three solid phases will react with water in a way similar to mixtures of any two binary phases can be determined only by experiment. For this reason we have regarded the reaction with water as an insufficient test of chemical individuality.

The essential problem for such a mixture of oxides is to determine the inter-relation of the phases of the ternary system. It was with this intent that the binary systems were first studied and it is hoped that the present paper may assist in clearing up the nature of cement clinker and perhaps aid in establishing more reliable standards, as well as better means of determining the quality of the commercial products.

OPTICAL STUDY.

For the satisfactory solution of the problems of equilibrium arising in any given physico-chemical system under different conditions three distinct lines of evidence—chemical, thermal, optical—are essential and usually adequate. Of these the first states the exact proportions of the chemical elements in the system, the second, the temperatures at which changes in the energy content of the system occur, the third, the different kinds of substances (crystals, glass) which are formed, their relative proportions in the mass (crystal composition), and their spacial relations (texture). These three lines of approach are not strictly independent, no one in itself being sufficient to solve the problems involved; they also overlap to some extent, the data from the one serving to corroborate and to supplement the results obtained by the other methods.

In the actual investigation of a system of crystalline substances and its behavior under different conditions, the first step is usually the determination of its chemical composition and of certain of its conspicuous physical properties, the second, to locate and interpret the changes, chemical or physical, which the system passes through on heating and cooling. Each change of state, either on further heating or on cooling, is accompanied by an absorption or release of a quantity of heat which can be detected by thermal methods and which thus defines the temperature limits within which the different crystals in the system are stable.

These substances are recognized and determined by use of the petrographic microscope. In any given preparation which has been subjected to a definite heat treatment, the optical properties of each one of the substances present are first ascertained separately and these suffice for the subsequent identification of the substance. If this be not done, the microscope is able merely to distinguish between the substances in the preparation, not to identify them. For this reason, it is necessary before undertaking the study of an involved chemical system, within which a number of different substances of unknown optical properties may be formed, to begin with the

simple systems which compose it and from which only one or two substances can possibly be formed. After these have been thoroughly investigated, and the properties of each substance definitely ascertained, the larger system may be approached with definite knowledge of the participating ingredients. This plan of attack has been followed in the study of the Portland cement problem.

Experience has shown that artificial preparations, especially silicates, are usually extremely fine-grained, and require, in consequence, special methods for their determination under the microscope. These methods have recently been developed and tested to such an extent that it is now possible to determine all of the essential optical constants of a single clear grain measuring only a few hundredths of a millimeter in diameter.

The products are examined ordinarily in the form of powder obtained by tapping (not rubbing or grinding) a small lump of the preparation with a pestle in an agate mortar. A small portion of such finely divided powder is conveyed to an object glass, where it is mounted in a liquid of known refractive index. Thin sections of the preparations are rarely made as the powder is better suited, for a number of reasons, to such determinative work; it can be prepared in a few seconds; it is easy to manipulate, a single grain which can be rolled about in the refractive liquid often serving for the determination of a number of the different optical constants; when immersed in a refractive liquid, whose index is equal to that of one of the phases present, this phase practically disappears, and the remaining phases acquire added prominence thereby, a condition which is especially useful in homogeneity tests. The use of the powder, however, precludes satisfactory studies of the textural features of a preparation. For this purpose, thin sections are well adapted, but in most equilibrium problems of this nature, the texture or spacial relations of the different phases are of subordinate importance and are usually disregarded. For the proper study of texture, relatively large furnace charges are required, too large in fact to serve satisfactorily for the thermal measurements.

For artificial silicate preparations whose granularity is expressed in hundredths of millimeters, the following methods have been found best adapted for the determination of the optical properties:

Refractive Indices.—In determinative work with artificial silicate preparations, the optical constants which are usually ascertained by actual numerical measurements are refractive indices, birefringence, optic axial angle, extinction angle, cleavage angle; the other optical features, such as crystal habit, color, pleochroism, absorption, optical character, dispersion of the bisectrices and of the optic axes, are usually ascertained by direct examination without numerical measurement. Of these optical characteristics, the most useful single feature is unquestionably the refractive index; and, fortunately for the observer, it is perhaps the easiest to determine with a high degree of accuracy. This is done by the im-

mersion method¹ whereby fine particles of the substance are mounted in a drop of a refractive liquid of known index. By using obliquely incident light or by observing the Becke line, it is possible to ascertain at a glance whether the refractive index of a particular grain is above, below, or about equal to that of the liquid. With a series of different refractive liquids² at hand, it is possible to determine the refractive index of a clear, isolated grain measuring only a few thousandths of a millimeter in diameter. The error of such a determination in ordinary rapid work should be less than ± 0.005 , while if monochromatic light be used and care taken to select clear single grains, the error may be reduced to ± 0.001 . If the grain be anisotropic, the three principal refractive indices, α , β , γ , are determinable by placing the grain in such positions that the plane polarized light waves from the lower nicol are transmitted parallel to one of the three ellipsoidal axes. From these three approximate values of α , β and γ , the birefringence and also the optic axial angle can be calculated roughly, both of which may then be checked by direct measurement on appropriate sections.

The chief difficulty in the measurement of the refractive indices of minute grains is one of mechanical subdivision; the grains occur frequently in fine overlapping aggregates, often embedded in glass; under these conditions it is not an easy task to find a clear, isolated grain on which satisfactory measurements can be made.

Birefringence.—The measurement of this property involves two separate determinations: (1) that of the thickness of the grain or plate under observation, and (2) that of the path difference of the transmitted light waves. The simplest method for measuring the thickness of a mounted plate or grain is to focus with a high power objective, first on its upper surface and then on its lower surface, as it appears through the grain or plate itself. The amount of movement of the fine adjustment screw during this operation is the apparent thickness of the plate or grain, provided, of course, that the fine adjustment screw is accurately constructed, which, unfortunately, is not the case in many microscopes. The true thickness is obtained by multiplying the apparent thickness

by the average refractive index of the plate. Experience has shown that under those conditions an error of 5 and even 10 per cent. is possible; especially if the plate be very thin; on thicker plates or grains the percentage error is correspondingly smaller. To insure greater accuracy the average of a series of determinations on the same plate should therefore be taken. The order of the interference color is ascertained by means of a Babinet compensator or of a graduated wedge constructed on the same principle, or of the interference color chart. If care be taken to select proper sections, the results should not be in error more than 10 per cent. and usually less, the numerical error being confined to the third decimal place.¹

Optical axial angles of small grains are most readily measured by means of the coordinate micrometer plate or the bi-micrometer ocular.² On favorable sections (0.025 mm. and over in diameter), the probable error of such measurements is about $\pm 1^\circ$ in case both optic axes appear in the field of vision, and $\pm 3^\circ$ in case only one optic axis is seen. For such measurements the particles should be immersed in a liquid of the refractive index corresponding to β to eliminate errors due to refraction on the uneven surfaces of the grains. In weakly birefracting substances and interrupted sections the axial bars are less sharply defined and the axial values obtained thereon are correspondingly less accurate.

The extinction angle is the angle between a given crystallographic direction and a definite optical direction on a specified crystal face and the accuracy with which it can be determined depends in part on the quality of the crystallographic development of the crystallite itself. By use of the bi-quartz wedge plate³ the position of total extinction can be determined on a single trial within $10'$ on favorable sections. If the crystallographic direction to which the particular extinction angle is referred be sharply defined, the extinction angle can readily be determined within $10'$ or less on crystallites measuring only 0.02 to 0.03 mm. in length.

Color, pleochroism and absorption can usually be determined, if sufficiently intense, on grains measuring 0.02 mm. and over, and in certain instances on still smaller particles.

The optical character can ordinarily be ascertained on grains 0.02 mm. and over in diameter; on sharply birefracting grains of small optic axial angle, 0.01 mm. diameter is sufficient for a satisfactory interference figure, while on very weakly birefracting substances 0.02 mm. diameter hardly suffices, owing to the indistinctness of the figure.

In observing interference figures from minute grains, it is essential that all extraneous light be excluded by means of a diaphragm⁴ in the image plane.

Other features, as *crystal habit, dispersion of the*

¹ O. Maschke, *Pogg. Ann.*, **145**, 565 (1872); Wiedemann's *Ann.*, **11**, 722 (1880). J. Thoulet, *Bull. Soc. Min. France*, **3**, 62 (1880). H. Ambronn, *Ber. Sächs. Gesell. d. Wissensch. Math. Phys. Kl.*, **1896**. J. L. C. Schroeder van der Koik, *Zeitsch. f. Wissen. Mikrosk.*, **8**, 458 (1898). Fred. E. Wright, *Am. J. Sci.*, [4] **17**, 385 (1904); *Tschern. Min. Petro. Mitt.*, **20**, 239 (1901).

² The following set of refractive liquids has recently been prepared in this laboratory and found satisfactory. It differs from previous sets in that the number of liquids employed is smaller and their dispersion relatively low. The chemicals were obtained from Merck and Company, New York, and the refractive indices measured on a total refractometer in sodium light. The liquids are conveniently kept in small dropping bottles with ground glass dropper and cap which interposes two ground joints to prevent evaporation. The set is so prepared that the refractive index of each successive liquid is 0.005 higher than the one preceding it. The mixtures are the following:

Refractive indices.	Liquids.
1.450–1.475	Mixtures of petroleum and turpentine.
1.480–1.535	Turpentine and ethylene bromide
1.540–1.635	Clove oil and α -monobromnaphthalene.
1.640–1.655	α -monobromnaphthalene and α -monochloronaphthalene.
1.660–1.740	α -monobromnaphthalene and methylene iodide.
1.745–1.790	Methylene iodide and sulfur.

³ For a detailed discussion of this method, see *Am. J. Sci.*, [4] **29**, 416 (1910).

² *Am. J. Sci.*, [4] **24**, 316–369 (1907); **29**, 423 (1910).

³ *Ibid.*, [4] **26**, 349–390 (1908); **29**, 424 (1910).

⁴ A satisfactory diaphragm for this purpose is described in *Am. J. Sci.*, [4] **29**, 412 (1910).

optic axes, and of the bisectrices, and the general correlation of optic and crystallographic properties, can occasionally be accomplished on isolated grains, 0.02 to 0.03 mm. in diameter, although for ease of manipulation and general accuracy, larger grains and sections are preferable.

It may be stated, as a general rule, that most of the optic properties can be determined with sufficient accuracy on grains measuring 0.02 to 0.05 mm. in diameter, and certain optical properties on still smaller particles.

THE COMPOUNDS.

In the following paragraphs a brief summary of the optic properties of the different compounds which occur in the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ diagram and which may appear in Portland cement, especially if it has not been thoroughly mixed, is given, special emphasis being placed on those features which are characteristic of each compound and serve to distinguish it from the others. The compounds of the binary series will be considered first, then the ternary compounds.

THE LIME-SILICA SERIES.

Calcium Oxide (CaO).—Lime appears usually in fine isotropic grains and clusters of grains, usually rounded in outline and of very high refractive index (about 1.83). In the powder preparation, free lime is easily recognized, even in particles measuring only a few thousandths of a millimeter in diameter, by its rounded shape, isotropism and high refractive index, the highest of any crystal in the diagram. Only one phase of free lime has been observed.

Silicium Oxide (SiO_2).—Silica, on the other hand, is known to crystallize in at least six different modifications, only three of which, however, appear at ordinary temperatures, the remaining phases being enantiotropic high temperature modifications of the first three.

α -Quartz.—In all Portland cement preparations, which have been heated to high temperatures, quartz can only appear in residual grains which have not been completely altered by the heating process. Above 800, quartz is unstable and changes into cristobalite, but the change is so sluggish that even at 1300° and 1400° it proceeds slowly and in certain instances of unequal treatment, particles of original quartz may still exist in the end product. They are then easily recognized as irregularly shaped, colorless pitted grains with average refractive index about 1.550, birefringence medium, uniaxial, optically positive.

α -Cristobalite occurs in the artificial preparations as cryptocrystalline aggregates, weakly birefracting and of refractive index about 1.485. These aggregates are so fine and overlap to such an extent that, except for the refractive index, it is not possible to measure the optical constants satisfactorily. Thermally, this mineral is interesting because of its inversion at about 225°. This inversion is sharply marked,

both on heating and cooling. On heating, the minute birefracting grains become suddenly dark (the β form being isometric and therefore isotropic) as the inversion temperature is reached, while on cooling, the reversion is marked by the sudden appearance of minute, star-like dots scattered over the field. Evidence of some superheating and of undercooling (10° to 20°) was noted.

α -Tridymite.—This mineral occurs likewise in fine cryptocrystalline aggregates, the individual units of which are so intergrown and overlap to such an extent that it is ordinarily not possible to isolate a single unit and to determine its properties. The average refractive index is about 1.478, a value slightly lower than that of cristobalite; in the absence of a determinable crystal form this is the chief distinguishing optical feature. Under the thermal microscope the minute grains and flakes are distinguishable from cristobalite by their inversion to β -tridymite at about 120°. β -Tridymite is hexagonal and weakly birefracting, so that basal plates appear isotropic above 120° while flakes on edge are distinctly birefracting and remain so even at high temperatures. In the absence of crystal form of the two substances, cristobalite and tridymite, the thermal microscope affords the most satisfactory method for distinguishing between the two.

The fact that cristobalite appears in nature as minute octahedra and tridymite in hexagonal flakes proves that their temperatures of formation were above 220° and 120° respectively.

Under normal conditions, neither of these minerals appears in Portland cement and their determination under the microscope is a matter of scientific rather than of practical interest.

Calcium Metasilicate (CaO.SiO_2) ($\text{CaO } 48.3, \text{SiO}_2 51.7$).—This compound appears in two forms, one (β - CaSiO_3) stable at temperatures below 1190°, and represented in nature by the mineral wollastonite; the other (α - CaSiO_3), pseudo-wollastonite, stable from 1190° up to the melting point and occurring only in artificial preparations.

α - CaSiO_3 .—This form crystallizes in equal grains without decisive crystal outline. Its distinctive optical features are refractive indices, $r = 1.650 \pm 0.002$; $a = 1.609 \pm 0.003$; birefringence strong, $r-a$ about 0.041; optical axial angle small, nearly uniaxial, optical character +.

β - CaSiO_3 , Wollastonite.—This compound occurs in elongated laths of medium to weak birefringence and parallel extinction, and similar in every respect to the natural mineral. Cleavage along the laths and fibers is well marked. The refractive indices are $r = 1.632 \pm 0.002$; $\beta = 1.628 \pm 0.003$; $a = 1.616 \pm 0.003$; $r-a$ about 0.015. Optical axial angle, $2E$ about 70°; optical character negative; plane of optic axes normal to the elongation of the laths.

3CaO.2SiO_2 ($\text{CaO } 58.2, \text{SiO}_2 41.8$).—This compound, from cristobalite resulting from the inversion of quartz heated to 1500°. Mallard's determination of 180° for this temperature is certainly too low. More accurate measurements of this inversion temperature are in progress and will be included in a paper to be published later of the different forms of SiO_2 and their relations to each other.

¹ This temperature, which is only approximately correct, was measured in the thermal microscope on a plate cut from a radial spherulite of cristobalite formed by crystallizing silica glass. The same value was obtained

like the tricalcic silicate, is not stable at its melting point but dissociates before that temperature is reached into a mixture of orthosilicate and metasilicate. It crystallizes in rounded irregular grains, without definite crystal outline and without distinct cleavage. The birefringence is not strong, γ - α being less than 0.01; the interference colors are usually gray of the first order and rarely reach first-order yellow. The refractive indices are approximately $\gamma = 1.650$ and $\alpha = 1.642$; the optic axial angle is large and the optical character positive. So far as the optical evidence goes, the crystal system may be orthorhombic.

It was at first thought that this substance might be pure äkermannite whose formula, according to Vogt, is $4\text{CaO} \cdot 3\text{SiO}_2$, but äkermannite is tetragonal and uniaxial and its refractive indices are γ about 1.640, α about 1.635. The presence of magnesia in äkermannite may account for the observed differences in the optical behavior between the two substances, if so the correct formula for pure äkermannite is $3\text{CaO} \cdot 2\text{SiO}_2$, and not $4\text{CaO} \cdot 3\text{SiO}_2$, as given by Vogt.

$2\text{CaO} \cdot \text{SiO}_2$ (CaO 65, SiO_2 35).—This compound crystallizes in four distinct forms, the α -form, stable above 1410° to the melting point, the β -form, stable between 675° and 1410° , the γ -form, stable below 675° . The β' -form is apparently a monotropic unstable form. With the exception of the α - and β -forms, these forms are noticeably different optically and their determination under the microscope is not a difficult matter. The α - and β -forms, however, are closely similar optically and often require careful optical work to distinguish between them.

γ - $2\text{CaO} \cdot \text{SiO}_2$.—This form is obtainable only as a fine powder which results from the inversion of the β -form and consequent dusting of the preparation due to the 10 per cent. volume increase at the temperature of change. The γ - $2\text{CaO} \cdot \text{SiO}_2$ is prismatic in habit with perfect cleavage along the prism axis; it is colorless and usually extinguishes parallel with the direction of elongation. Indications of twinning lamellae parallel with the cleavage were observed occasionally, showing low extinction angles not exceeding $c : \epsilon = 3^\circ$. Ordinarily the extinction is parallel. The refractive indices are $\gamma = 1.654 \pm 0.003$, $\beta = 1.645 \pm 0.003$; $\alpha = 1.640 \pm 0.003$. The birefringence is medium, about 0.015. The optic axial angle $2E$ is about 52° . The plane of the optic axes is normal to the cleavage direction.

β - $2\text{CaO} \cdot \text{SiO}_2$.—The crystallites of this form are prismatic in shape with cleavage parallel to the prism axis. They are colorless, apparently orthorhombic in crystal system. The least ellipsoidal axis is parallel to the prism axis. The optic axial angle is very large. The refractive indices are high, α being about 1.72 and γ about 1.735. The birefringence is medium, the interference colors in the fine powder rarely exceeding blue of the second order. This form is readily distinguished from the γ -form by its higher refractive index and the position of the plane of optic axes which is parallel to the cleavage direction.

α - $2\text{CaO} \cdot \text{SiO}_2$.—Like the β -form, this form shows prismatic development with good cleavage parallel

with the prism axis. The crystals are usually so intricately intergrown that a satisfactory measurement of their different optical constants is exceedingly difficult. Twinning is a characteristic feature of this form and is often extremely complicated. Different sets of the twinning lamellae occur intersecting at various angles, and, together, form an interpenetrating mass not unlike microcline or leucite. Extinction angles along the prism axis were noted as high as $c : \alpha = 18^\circ$, though smaller angles are more frequent. The hardness is between 5 and 6. The refractive indices are approximately $\alpha = 1.714$; $\beta = 1.720$; $\gamma = 1.737$; birefringence about 0.023; optic axial angle very large; optical character positive. The plane of the optic axes is about parallel with the direction of elongation of the crystals.

β' - $2\text{CaO} \cdot \text{SiO}_2$.—This apparently unstable form occurs in fine equant grains, colorless and without cleavage. The average refractive index is about 1.715, almost exactly that of the tricalcic silicate. The birefringence is also very weak. Interference figures are difficult to obtain because of the fine granularity and the weak birefringence, but the optic axial angle appears to be small or zero and the optical character positive. This last characteristic is the most important feature which serves to distinguish this form from the tricalcic silicate.

$3\text{CaO} \cdot \text{SiO}_2$ (CaO 73.59, SiO_2 26.41).—This compound, which is not stable at its melting point, but changes into a mixture of free lime and orthosilicate at higher temperatures crystallizes in small equant grains, colorless and apparently without cleavage. The average refractive index is approximately 1.715; and the birefringence is very weak, not over 0.005. Interference figures are difficult to obtain because of the weak birefringence and the fineness of the grains, which rarely measure over 0.03 mm. diameter. The grains appear uniaxial or biaxial with small optic axial angle and are optically negative. On some of the preparations cut nearly normal to the optic axis, especially on those from preparations containing a little Al_2O_3 , fine twinning lamellae were observed with low extinction angles indicating possibly that the crystal system is monoclinic. The distinguishing optical features of this compound are equant development, lack of cleavage, weak birefringence, optically negative character with $2E$ small or zero, and refractive index about 1.715. It is an interesting fact that in preparing this compound from the mixed oxides at 1400° or 1500° , the compounds, free lime and orthosilicate, are first formed and these then in turn unite to form the tricalcic silicate on longer heating.

THE $\text{CaO-Al}_2\text{O}_3$ SERIES.

In this series the compounds which have been observed are CaO , $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, two forms of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, the one stable, the second unstable, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, two forms of $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$, a stable form and an unstable form, and Al_2O_3 . The distinguishing optical features of these different forms are briefly:

$3\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CaO 62.22, Al_2O_3 37.78).—This compound is not stable at its melting point and perfectly

homogeneous preparations of this composition, free from grains of crystallized CaO and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, have never been obtained. It occurs in equant grains, often hexagonal or rectangular in outline with indications of imperfect cleavage after the octahedron or rhombic dodecahedron. The fracture is conchoidal and the hardness about 6. The grains are colorless and isotropic, of vitreous luster, with refractive index $n_{\text{Na}} = 1.710 \pm 0.001$. Occasionally faint gray interference colors were observed on certain grains and were evidently due to strain. This compound crystallizes well in comparatively large isometric grains measuring up to 0.1 mm. in diameter.

$5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (CaO 47.78, Al_2O_3 52.22).—The stable form of this substance crystallizes in the isometric system. Under the microscope it appears in equant grains without definite crystal outline or distinct cleavage. The luster is vitreous and the fracture conchoidal and often interrupted. The hardness is about 5. The refractive index is $n_{\text{Na}} = 1.608 \pm 0.002$. The refractive index of the glass of the same composition is about 1.662, a value considerably higher than that of the crystals.

Unstable $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$.—This form is obtained only under special conditions of cooling, and is usually not well developed in single crystallites, but occurs as radial spherulites or aggregates of overlapping, and often approximately parallel fibers. The crystal habit is fibrous to prismatic; cleavage if present is parallel with the fiber direction but is far from perfect. The luster is vitreous and the color usually green, due possibly to a slight admixture of platinum from the crucible. The hardness is about 5; the refractive indices are, approximately, $\alpha = 1.687 \pm 0.002$; $\gamma = 1.692 \pm 0.002$. The birefringence is weak; the optic axial angle is apparently large and the optical character apparently negative but not easy to determine satisfactorily because of the aggregate effect of superposed fibers. The plane of the optic axes and the extinction are parallel with the fiber direction. Some of the more deeply colored grains are pleochroic with α = blue-green, ϵ = olive-green. Absorption $\alpha > \epsilon$. These properties indicate that this form is orthorhombic in crystal system. Its distinguishing features are refractive index about 1.69, birefringence weak and tendency to fibrous development.

$\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CaO 35.44, Al_2O_3 64.56).—So far as observed this compound occurs only in one form. It crystallizes readily in prismatic to fibrous aggregates, the individual crystals of which are difficult to isolate. Twinning is a characteristic feature and is especially prominent on sections nearly normal to the acute bisectrix. Such sections are intricately divided into a hexagonal meshwork of interlocking sextants which extinguish in different positions. Cleavage parallel with the fiber direction is occasionally indicated but is not perfect. The hardness is about 6.5, luster vitreous and extinction often oblique. The refractive indices are $\gamma = 1.661 \pm 0.002$; $\beta = 1.654 \pm 0.003$; $\alpha = 1.641 \pm 0.002$. The birefringence is fairly strong, about 0.02. The optic axial angle, $2V$ is fairly small and about $36^\circ \pm 4^\circ$. The

crystal system is either monoclinic or triclinic, and probably monoclinic.

$3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$ (CaO 24.78, Al_2O_3 75.22).—The stable form of this compound is uniaxial and possibly tetragonal in crystal system. It crystallizes in equant grains and is readily recognized under the microscope by its strong birefringence and uniaxial, optically positive character and ordinary refractive index, about 1.617. Cleavage, if present, is poor. The hardness is about 6.5; the luster vitreous. The refractive indices are $\omega = 1.617 \pm 0.002$, $\epsilon = 1.651 \pm 0.002$; the birefringence $\epsilon - \omega$ is about 0.032. The uniaxial interference figure is sharply defined and easy to obtain, even on grains measuring not over 0.01 mm. in diameter. The grains often contain fine thread-like inclusions of a higher refracting, weakly birefracting to isotropic substance which are too fine for satisfactory determination. Their total amount is very slight but nevertheless appreciable.

The unstable form of this compound inverts so readily to the stable form that perfectly homogeneous preparations could not be obtained. Its crystals are prismatic in habit and show under the microscope fair prismatic cleavage. Their luster is vitreous and their hardness about 5.5 to 6. The refractive indices are, approximately, $\gamma = 1.674 \pm 0.002$; $\beta = 1.671 \pm 0.002$; $\alpha = 1.662 \pm 0.003$. The birefringence is medium, $\gamma - \alpha$ being about 0.013. The optic axial angle is not large, $2V = 35^\circ \pm 5^\circ$. The axial dispersion is strong, $2V_r$ being greater than $2V_v$. This form is probably orthorhombic in symmetry. Its chief characteristics are, average refractive index about 1.67, medium birefringence, small negative optic axial angle with strong axial dispersion; the plane of the optic axes and the ellipsoidal axis are parallel with the direction of prismatic elongation.

Al_2O_3 , *Artificial Corundum*.—The optic properties obtained on fine-grained preparations of this composition agree well with those of the natural mineral. In the fine granular aggregates, crystal outlines were rarely observed, the individual grains being less than 0.05 mm. in diameter and rounded in outline. Minute air cavities were abundant and characteristic. The hardness is 9. The refractive indices are $\omega = 1.768 \pm 0.003$; $\epsilon = 1.760 \pm 0.003$; the birefringence is fairly weak, $\omega - \epsilon$ being about 0.009. The grains are uniaxial and optically negative. From mixtures with other oxides, corundum usually crystallizes in the form of thin, sharply-defined, hexagonal flakes.

THE Al_2O_3 - SiO_2 SERIES.

Only one compound has been observed in this series, $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, which occurs in nature in three distinct forms, sillimanite, andalusite and cyanite. Notwithstanding repeated efforts to obtain them, the last two forms, andalusite and cyanite, have not been formed with certainty in this laboratory. The mineral dumortierite ($4\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) which occurs in nature in pegmatites was not obtained from the artificial melts.

$\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ (Al_2O_3 62.85, SiO_2 37.15).—This compound crystallizes from the melt with great rapidity on cooling and, as a result, the preparations obtained

are in general too fine-grained for accurate determinations. The crystallites are fibrous and lath-shaped, and, like the natural mineral sillimanite, are often in close parallel groups. Terminal sections of the fibers are square in outline, weakly birefracting and extinguish parallel with the diagonals of the rectangles. In the center of nearly every section a minute inclusion is present, often in the shape of a cross, the arms of which are parallel with the sides. The refractive indices which were determined by the immersion method are noticeably lower than those of the natural minerals, a fact for which no explanation has yet been found. $a = 1.638 \pm 0.003$; $\beta = 1.642 \pm 0.003$; $\gamma = 1.653 \pm 0.003$; the birefringence is medium, $\gamma - a$ being about 0.014. The optic axial angle is not large, $2V$ being apparently between 40° and 75° ; the optic character is positive, and the acute bisectrix lies in the direction of elongation of the fibers. Cleavage, parallel with the fiber direction, is well marked. Minute inclusions of a lower refracting isotropic substance (n. about 1.530) occur frequently in the artificial sillimanite preparations and may possibly be glass. These inclusions are almost invariably present in small amounts and no satisfactory explanation has been found for their occurrence.

THE TERNARY COMPOUNDS.

In nature, a number of minerals occur which are essentially calcium-aluminium silicates. They are found chiefly in metamorphosed limestones, usually near eruptive contacts, and, except for anorthite and possibly gehlenite, do not appear to be stable at their melting temperatures and do not crystallize, therefore, from melts of their own composition. In this list belong spenoclas (6CaO.Al₂O₃.6SiO₂), grossularite (3CaO.Al₂O₃.3SiO₂), meionite (4CaO.3Al₂O₃.6SiO₂), and possibly gehlenite (3CaO.Al₂O₃.2SiO₂). Anorthite (CaO.Al₂O₃.2SiO₂), on the other hand, and the compound 2CaO.Al₂O₃.SiO₂ and another compound whose composition has not yet been definitely determined, crystallize as such from melts of their own composition and are stable.

CaO.Al₂O₃.2 SiO₂ (CaO 20.1, Al₂O₃ 36.7, SiO₂ 43.2). *Artificial Anorthite*.—This substance appears in the preparations either in lath-shaped individuals elongated after the edge (001) (010) or as tabular crystals after the side pinacoid M (010). It crystallizes readily and if given time to grow at high temperatures not far below the melting point, its crystals attain fair size) 0.1 mm. and over in diameter), and are readily recognized under the microscope. The refractive indices are $\gamma = 1.589 \pm 0.001$, $\beta = 1.585 \pm 0.001$, $a = 1.576 \pm 0.001$, values which are identical within the limits of error with those of natural anorthite. The birefringence is not strong and the interference colors in the small grains are confined usually to the first order. The optic axial angle is large; and the optical character, negative. The extinction angle on the basal pinacoid is approximately 35° . More accurate measurements of the optic properties of anorthite as well as of other members of the plagioclase series are in progress. Anorthite is so far distant from the Port-

land cement composition that it is not likely to appear in cement clinkers but, if so, it is easily recognized by its relatively low refractive index about 1.585, its medium birefringence and its polysynthetic twinning with large extinction angles.

2CaO.Al₂O₃.SiO₂.—(CaO 40.83, Al₂O₃ 37.19, SiO₂ 21.98).—This compound crystallizes readily and in fair-sized grains. The crystallized pure melt is glassy in appearance and the individual crystals are transparent. Cleavage after the base is distinct but not perfect. Fracture conchoidal. Hardness about 6. Specific gravity about 3.038. The refractive indices for sodium light are $\omega = 1.667 \pm 0.002$, $\epsilon = 1.658 \pm 0.002$. The birefringence is not strong and the interference colors are confined usually to the first order. A pronounced yellow interference color is not uncommon but is not sufficiently marked to serve as a distinguishing feature. The compound is uniaxial and optically negative. Interference figures are easy to obtain because of the basal cleavage and usually exhibit only the black cross. Basal sections often show indications of rectangular outline and the crystals may possibly be tetragonal.

In its optical characteristics this compound resembles the mineral gehlenite closely. The cleavage, optical character and crystal habit of the two are practically identical while their refractive indices and birefringence are only slightly different. The chemical formula of gehlenite (3CaO.Al₂O₃.SiO₂ or CaO 42.9, Al₂O₃ 26.2, SiO₂ 30.9), which is usually given in the text books, does not agree, however, with that of the above compound. Only a few careful chemical analyses of gehlenite have been made and these vary within wide limits. It may be possible, but not probable, that solid solution in the natural mineral plays an important part and changes its composition accordingly. In the light of present evidence, however, the conclusion that the new compound (2CaO.Al₂O₃.SiO₂) is artificial gehlenite is hardly warranted.

It should be stated that the preparations of this composition, 2CaO.Al₂O₃.SiO₂, was never perfectly homogeneous but always contained small amounts, up to 1 per cent., of a lower refracting substance, apparently isotropic and appearing as fine threads and patches in the grains. No decisive determination of these threads could be made, although in certain instances they appeared to be noncrystallized glass.

SUMMARY.

The Binary Systems.—In the earlier work with mixtures of pure lime and silica, two compounds, the metasilicate (CaO.SiO₂) and the orthosilicate (2CaO.SiO₂) were definitely established but no trace of the hitherto generally accepted tricalcic silicate could be found in mixtures of the pure lime and pure silica. In the three-compound system on the other hand, the tricalcic silicate appears promptly with the addition of alumina to mixtures of appropriate lime-silica concentration, and after a long and difficult experimental investigation, involving the study of about 1000 heat treatments of various compositions, many of which required to be studied at temperatures between

1800 and 1900° C., it has finally been prepared pure excepting for a small excess (between 1 and 2 per cent.) of orthosilicate or lime or both.

Tricalcic silicate appears to be unstable at its melting temperature, and so does not form from a melt of this composition. For the same reason, it does not form eutectics with the adjacent compounds, calcium orthosilicate and lime. Neither is there any evidence that the tricalcic silicate takes up calcium orthosilicate or lime in solid solution.

In addition to the tricalcic silicate a new and probably unstable form of the orthosilicate has been discovered which may prove to be of importance in Portland cement.

The Ternary System.—The general boundaries of the different phases occurring throughout the entire diagram of the ternary system, $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, have been established, together with the course of the boundary curves. From these it is possible to predict the compounds which will crystallize out of a lime-silica-alumina cement of any composition, provided only that the compounds are intimately mixed and the heat is sufficient to bring the mixture to equilibrium during formation. The exact location of the quintuple points with the exception of points 13 to 17 and the isotherms remain to be established. The location of these quintuple points is as follows:

Point.	17.	16.	15.	14.	15.
CaO.....	59.5	58.5	52.8	49.2	48.5
Al ₂ O ₃	32.5	33.0	40.5	44.0	42.0
SiO ₂	8.0	8.5	6.7	6.8	9.5

Portland cement clinker within the concentration limits set by Richardson *when in equilibrium* may exist in the following combinations, depending primarily upon relatively small changes in the quantity of lime present.

I.	II.	III.	IV.	V.
CaO	3CaO.SiO ₂	2CaO.SiO ₂	2CaO.SiO ₂	2CaO.SiO ₂
3CaO.SiO ₂	2CaO.SiO ₂	3CaO.Al ₂ O ₃	5CaO ₃ .3Al ₂ O ₃	2CaO.Al ₂ O ₃ .SiO ₂
3CaO.Al ₂ O ₃	3CaO.Al ₂ O ₃	5CaO.3Al ₂ O ₃	CaO.Al ₂ O ₃	CaO.Al ₂ O ₃

Richardson's typical cement corresponds to Class II. The relative cement-forming value of the above mixtures has yet to be determined. The more intimate the mixture of the raw material, and the more uniform the heat treatment, the closer will be the approach to equilibrium and therefore to constant relations and the more uniform the behavior of the final product. Classes III and IV are predicted from the general direction of the boundary curves and the quintuple points 14 and 15. Class V will occur in cements low in lime and will differ only in the relative amounts of the different phases from pure slag cements whose compositions lie below the line joining the calcium orthosilicate and $2\text{CaO}.\text{Al}_2\text{O}_3.\text{SiO}_2$ compositions. Type V is dependent on the nature and location of point 13 and is to be regarded as tentative.

If solid solutions are formed, they are very limited in extent and are not sufficient to affect the optical properties of either silicate, the lime or the aluminate. This fact serves to give greater definiteness to the problem and an unexpectedly clear field for studies of the cement-forming quality of clinkers of nearly related composition but different chemical constitution. It

therefore seems inevitable that such studies will lead to more reliable standards in cement practice.

The diagram indicates that the constitution of slag cement will be seriously affected by relatively small differences of composition in the neighborhood of the line joining the compounds calcium orthosilicate and $2\text{CaO}.\text{Al}_2\text{O}_3.\text{SiO}_2$ (Fig. 5). It is, however, unwise to draw positive conclusions about the character of this portion of the diagram until it has been more carefully studied.

Incidentally, it has been observed that Fe_2O_3 appears *not* to form solid solutions with CaO , $3\text{CaO}.\text{SiO}_2$, Ca_2SiO_4 , or $3\text{CaO}.\text{Al}_2\text{O}_3$. It does appear to react in some way with $5\text{CaO}.\text{Al}_2\text{O}_3$ but the nature of this reaction has not yet been studied. Attention should also be called in passing to the important fact that Fe_2O_3 dissociates at about 1400° with the formation of Fe_3O_4 —a fact which seems to have been overlooked by some investigators.

Finally, too great importance cannot be given to the constant use of the microscope in cement study and practice. It is not improbable that microscopic examination will eventually provide much of the formation desired about the constitution of test samples, with the advantage over chemical methods of giving immediate results.

GEOPHYSICAL LABORATORY,
CARNEGIE INSTITUTE, WASHINGTON,
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METHODS FOR TESTING COAL TAR AND REFINED TAR, OILS AND PITCHES DERIVED THEREFROM.

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The tests described in this article are not put forward as methods for the scientific examination of, or research into, the products of coal tar. An attempt has been made by a committee of chemists of this Company to revise and standardize the every-day tests applied to the raw materials and products of the American tar distiller. The primary object of this undertaking was that concordant results might be obtained by the operators in the Company's own laboratories. It is well known to those who have engaged in the testing of tar, pitch, creosote oil, etc., that results are absolutely not comparable in most cases unless both analysts have used the same methods. Even then, great care is necessary to eliminate the personal element. The foregoing is much more applicable to these physical tests of complex hydrocarbons, than it is to strictly chemical analyses, which involve definite reactions and are calculated according to formulae.

It is now over a year since these methods were adopted for use in our laboratories and the results have been encouraging. Many of the tests, particularly those of pitch, refined tar and creosote oil, are of interest to the consumer as well as to the producer. In response to many requests from time to time we have furnished copies of certain tests to chemists and engineers who desired them. The melting-point test

for pitch may fairly be called standard for designating and testing pitches throughout the country. The tests of creosote oil include the methods of the American Railway Engineering and Maintenance of Way Association, which are widely used by consumers of creosoted materials, and the methods of the United States Department of Agriculture, with slight modifications.

The tests are now described and illustrated in detail, in the belief that it will be a help to some who are called upon to test, or draw specifications for testing, materials concerning which little information is available in text-books. It is not supposed that the methods are the best possible in every instance. In some cases concessions have been made to precedent, in others to convenience. They will undoubtedly be revised from time to time as valued suggestions come to us from the rapidly increasing number of chemists who are engaging in the examination of these materials.

NOTE.—Apparatus marked "Special" or "Standard" on drawings is made up to our order and we will advise any one interested where such apparatus may be obtained.

TAR.

(a) Water in Tar.

The apparatus used is illustrated in Drawing No. 1. Measure 50 cc. of coal tar naphtha or light oil (which must be tested to determine that it is free from water, whenever a new supply is required) in a 250 cc. measuring cylinder. (No objection is raised to measuring

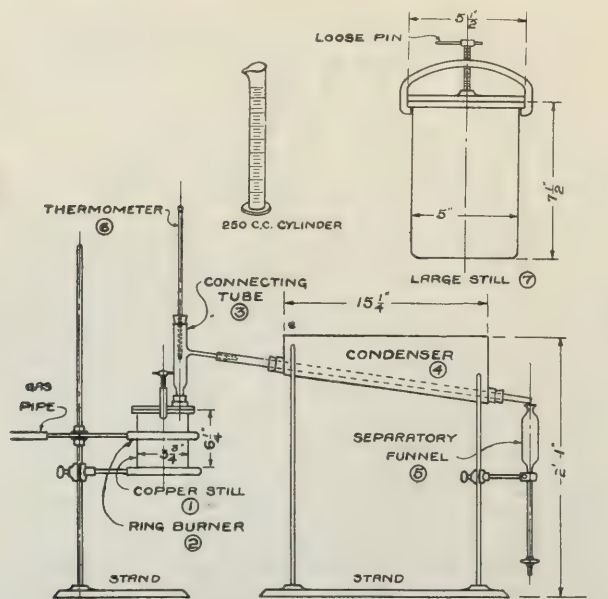
the still. Attach lid and clamp, using a paper gasket and set up apparatus as shown in drawing No. 1. Apply heat by means of the ring burner and distil until the vapor temperature, as indicated by the thermometer (in this and all other tests care must be used to have thermometer set exactly as shown in drawings) has reached 205°C . (401°F). The distillate is collected in the separatory funnel, to which 15–20 cc. of benzol has been previously added. This effects a clean separation of the water and oil. The reading is made after twirling the funnel and allowing to settle for a few minutes. The percentage is figured by volume.

(b) Specific Gravity.

The tar is dried by taking 300–400 cc. in the apparatus used for water determination without the addition of naphtha. The distillation is carried to 170°C . (338°F) vapor temperature. Any oil which has distilled over is separated from the water and returned to the still and thoroughly mixed in after cooling. Apparatus: a specific gravity bottle, Hubbard type (special), whose water capacity at 15.5°C . (60°F .) has been determined by experiment. 10 grams of tar are introduced at a temperature of $40\text{--}50^{\circ}$ into the weighing bottle and the weight taken after cooling. Then freshly boiled distilled water is added and the bottle kept in a bath at 15.5°C . (60°F .) until no further contraction takes place. The water is then adjusted to the mark and the bottle removed from the bath and weighed. Weight of tar divided by the weight of H_2O displaced gives the specific gravity. For rough determination, as of wet tar, a spindle may be used at any convenient temperature. To reduce the gravity as found to 15.5°C ., 0.000685 is added for each degree C., above 15.5°C . (or 0.00038 for each degree F. above 60°F .)

(c) Free Carbon.

Apparatus is shown in Drawing No. 2. Tar dried as under specific gravity must always be used. The dried tar is passed through a 30-mesh sieve to remove any foreign substances. In testing tars of 5 per cent. or more carbon content 5 grams are taken. On lesser percentages 10 grams are used. The amount is weighed out into a 50 cc. beaker and digested with c. p. toluol on the steam bath. Two 15 cm., 575 S. and S. filter papers, the inner one cut to 14 cm. diameter, are folded around a rod of about 1.5 cm. diameter, so as to form a long cylindrical filter cup. (These filter papers have been previously extracted with benzol to render them fat-free.) The cup is dried at $100\text{--}110^{\circ}\text{C}$. and placed in weighing bottle and weighed after cooling. It is supported by a wire or some convenient method over a beaker. The toluol tar mixture is now decanted through this cup and the beaker washed with hot toluol until clean, all washings being passed through the cup. (A convenient "policeman" to use in cleaning the beaker is a stout chicken feather trimmed so as to have a small fan at the end.) The filtrate should be carefully examined for any particles of free carbon and if there is any evidence of same, should be refiltered. Finally the cup is washed two or three times with hot c. p. benzol and then is



DRAWING No. 1
CRUDE TAR DISTILLATION
No. 1—COPPER STILL, SMALL SIZE SPECIAL
No. 2—RING BURNER " " "
No. 3—CONNECTING TUBE " " "
No. 4—CONDENSER WITH TUBE " " "
No. 5—SEPARATORY FUNNEL " " "
No. 6—THERMOMETER STANDARD
No. 7—LARGE STILL FOR COMPLETE TAR TEST SPECIAL
No. 8—RING BURNER, LARGE SIZE, SPECIAL (NOT SHOWN)

the tar direct into the still or in other ways, but the measurement *must* be made as described in case of dispute.) Add 200 cc. of the tar. Transfer contents of cylinder to copper still and wash the cylinder with 50–75 cc. more of naphtha, adding the washings to contents of

transferred to the extraction apparatus (see Figs. 1 and 2), the filter cup being supported by a wire (Fig. 3). C. P. benzol is used as a solvent, heat being applied by a steam bath and the extraction is continued a number of hours until the descending benzol is

Ash.—Take 10 grams in an open platinum or porcelain crucible and incinerate to constant weight by any convenient method, being careful to avoid foaming at the start or carrying off of ash at the end.

(e) *Viscosity.*

The Engler viscosimeter is used and time of flow of 200 cc. at 60° C. (140° F.) is taken. All directions for use of viscosimeter accompany the apparatus (E. & A. 7167, p. 393).

DISTILLED TARS.

Saturating Mixtures, Tarvia, Coatings.

A. *Specific Gravity.*—(Same as Tar.)

B. *Free Carbon.*—(Same as Tar.)

C. *Viscosity.*—

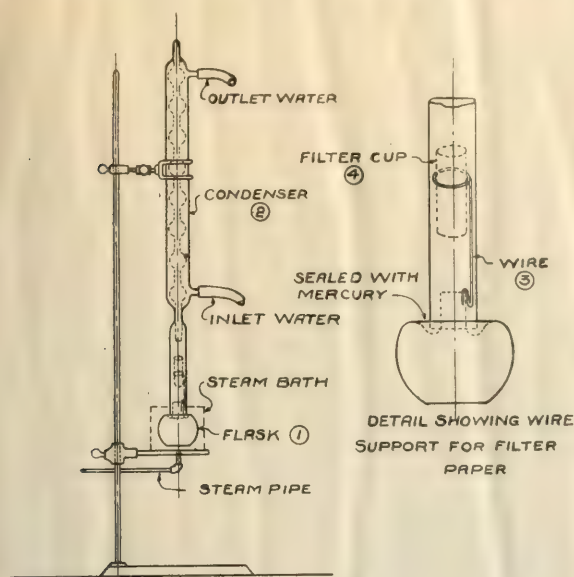
1. Saturating and light tarvias—Engler viscosimeter (same as Tar.)

2. Tarvia X to soft pitch—Schutte Penetrometer, Drawing No. 5.

The tests on the Schutte Penetrometer shall be made as follows:

The plug used shall be of the following dimensions: diameter, $\frac{5}{8}$ of an inch; height, 1 inch.

In filling the plug, it shall be placed upon a flat tin roofing disc, which has been greased with vaseline.



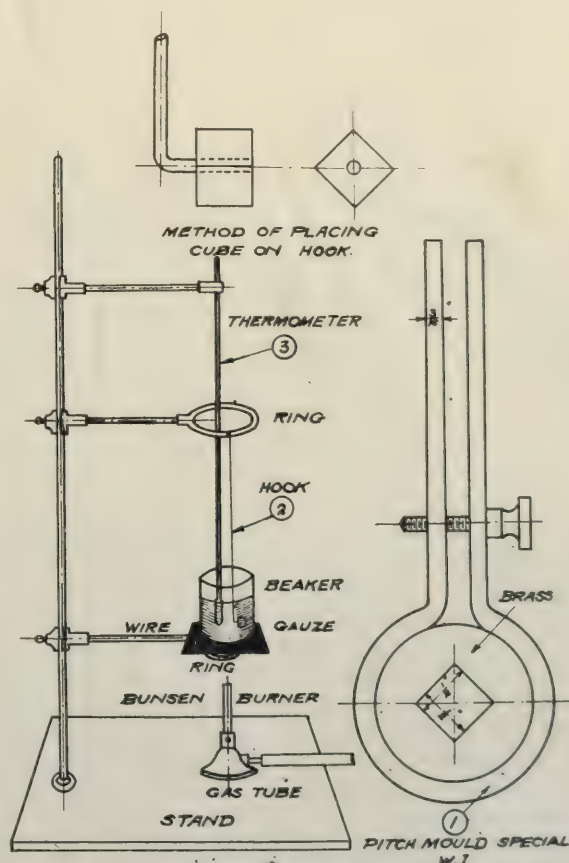
DRAWING No 2
EXTRACTION APPARATUS FOR FREE CARBON
No 1- FLASK (E & A 3185A or 3185C)
No 2- KNORR EXTRACTION APPARATUS E & A 3185
No 3- WIRE, COPPER AS PER SKETCH
No 4- FILTER CUP, 2 SHEETS C.B. & S 573
PREPARED AS DESCRIBED

completely colorless. The cup is then removed, dried as before, and weighed in the bottle after cooling. The balance used for the above determination should be accurate to 0.5 mg. In removing the filter papers from the extractor care should be taken that no particles of mercury find their way into the precipitate. To prevent splashing the filter paper should be elevated as near to the outlet of the condenser as possible. A good precaution is to cover the top of the filter cup with a round cap of filter paper.

(d) *Fixed Carbon and Ash.*

Fixed Carbon.—Based on report of Committee on Coal Analysis.¹ Place 1 gram of tar in a platinum crucible having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes by the watch. The crucible should be supported on a platinum triangle with the bottom 6 to 8 cm. above the top of the burner. The flame should be fully 20 cm. high when burning free, and the determination should be made in a place free from drafts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. To find "volatile combustible matter" subtract the per cent. of moisture from the loss found here. The residue in the crucible minus the ash represents the coke or fixed carbon.

Previous to applying the full heat of the Bunsen flame for seven minutes, as above described, the tar should be gently heated for a few minutes until the tendency to foam is passed.



DRAWING No 3
MELTING POINT TEST
No 1 PITCH MOULD (SPECIAL)
No 2 HOOK; MAKE OF 1/2 COPPER WIRE
No 3 THERMOMETER (SPECIAL)

The material shall then be poured in and the plug placed in water of the required temperature, for at least ten minutes. The plug shall then be screwed into the

¹ J. Am. Chem. Soc., 21, 1116, 1899, et seq.

tube while the tube is in position, and the plug submerged in the water. The tube shall be filled with water of the given temperature, and the disc removed by slipping it sideways. The time shall be taken from the moment of slipping off the disc. Extreme care must be taken to take the temperature accurately and keep the water at the given temperature within $\frac{1}{2}$ of a degree. An accurate thermometer shall be used. The water in the tank shall barely cover the shoulder of the tube. If care is taken to keep accurate temperatures, and the test is made with skill, successive determinations should agree within five seconds.

D. Distillation.—As under standard creosote method (see Creosote).

Temperature and fractions are to be taken as required.

PITCH.

A. Specific Gravity.—On soft pitch this is taken in a bottle as described under tars. On hard pitch an alternative method is suspension of a lump from the balance beam by a thread and noting the weight in air and water, being careful to remove any air bubbles found on the lump.

B. Free Carbon As in Tars.—

1. If pitch is hard enough it should be ground.
2. The carbon residue should be examined for foreign matter.

C. Melting Point.—Apparatus shown in Fig. 3.

1. Pitches from 43° – 77° C. (110° – 170° F.). A clean-shaped $\frac{1}{2}$ -inch cube of the pitch to be formed in the mold, placed on the hook of No. 12 copper wire, and suspended in the 600 cc. beaker so that the bottom of the pitch is 1 inch above the bottom of the beaker. (A sheet of paper placed on bottom of beaker and conveniently weighted will prevent pitch from sticking to the beaker when it drops off.) The pitch to remain five minutes in 400 cc. of water at a temperature of 15.5° C. before heat is applied. Heat to be applied in such manner that the temperature of the water is raised 5° C. (9° F.) each minute. The temperature recorded by the thermometer at the instant the pitch touches bottom of beaker to be considered the melting point.

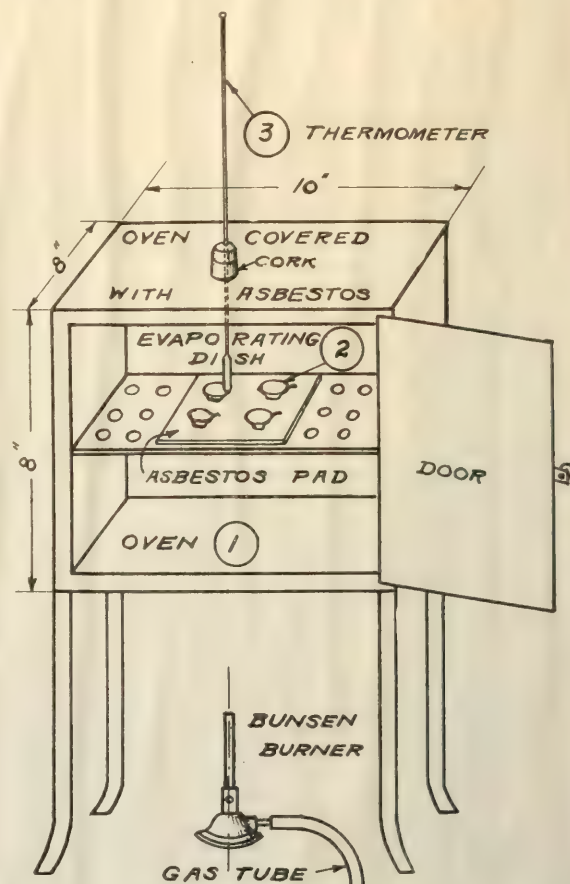
2. Below 43° C. (110° F.) the same method can be used except that at the start the water should have a temperature of 4° C. (40° F.).

3. For pitches from 77° C. up (170° F.), cottonseed oil should be substituted for water; otherwise the method remains the same. With these harder pitches, it may be necessary to heat the pitch in order to form a cube. Care should be used not to heat it any higher than is necessary, or to continue heating it for any length of time. A hot knife blade will often assist this manipulation.

NOTE.—To aid the removal of the pitch from the mold it may be greased with a very thin film of vaseline.

D. Breaking Point.—Apparatus, Fig. 5, Figs. 1 and 2. A small piece of pitch is quickly melted directly on the copper disc on the steam bath to a layer of about $\frac{1}{32}$ of an inch. The disc is then placed

in the porcelain dish and well covered with water of about 10° – 12° C. above the breaking point of the pitch. The temperature is reduced 1° per minute and tested from time to time by inserting a small, thin knife blade below the pitch and turning slightly until a point is reached at which the pitch snaps. This is taken as the breaking point. The copper disc should be held with a pair of tongs and not with the fingers.



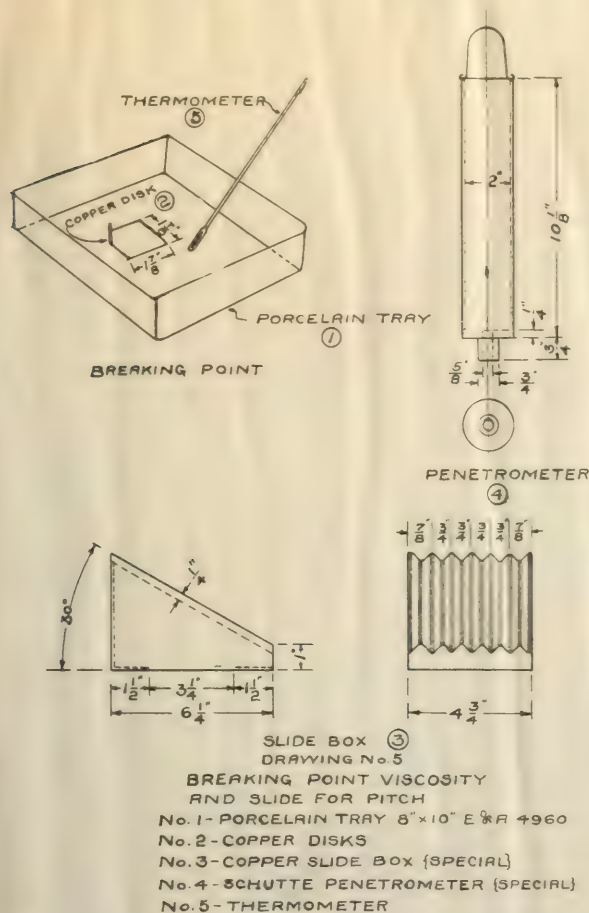
—DRAWING NO. 4.—
 DRYING & EVAPORATING OVEN.
 NO. 1—8½x8x10" DRYING OVEN EJA 3030
 ASBESTOS COVERED
 NO. 2—DISHES—EJA 2976-2" DIA (SPECIAL)
 NO. 3—THERMOMETER—STANDARD.

E. Evaporation Test.—Apparatus as shown in Drawing No. 4. The oven should have the top and sides covered with $\frac{1}{8}$ -inch asbestos. The shelf is provided with a $\frac{1}{4}$ -inch asbestos pad, large enough to accommodate the dishes. The bulb of the thermometer should be 1 inch above the shelf and the emergent stem must be within 10° C. of 100° . Not more than 4 tests should be run in the oven at a time. 10 grams of pitch are weighed in the dish, placed in the oven and held exactly at 160° C. for seven hours and after cooling in a desiccator, the loss in weight is noted.

When accuracy is required the apparatus used shall be a circular oven of the type described in Eimer & Amend's catalog No. 2073 D, having double walls, circulating fan and self-contained burner.

F. Slide Test.—Apparatus as in Drawing No. 5.

Fig. 3. A $\frac{1}{8}$ -inch cube of pitch, such as used for the melting point, is placed at the top of a depression in the corrugated plate (angle 30°) and warmed slightly and pressed down so as to present a rounded top, care being taken to keep the front edge intact. A mark



is made on the adjoining ridge parallel to the front edge of the cube. The slide plate is placed in an oven with a thermometer about 1 inch above the center of the slide and kept at 40° C. for seven hours. The measurement is taken from the previous mark to the furthest point the pitch has reached.

NOTE.—Soft pitches which run beyond end of slide must be watched and the time they slide to the end noted.

G.—Fixed carbon as in tar.

H.—Ash as in tar.

LIGHT OIL.

A. *Specific Gravity*.—Taken with a hydrometer at 15.5° C. For this and subsequent tests it must be dried if containing more than 1 per cent. of water. This is done as described under creosote.

B. Distillation.—Apparatus as in Drawing 8. 100 cc. are measured in a cylinder and transferred to the 200 cc. Jena glass distilling bulb and heated. The distillate is collected in a 100 cc. cylinder. The point where the first drop falls from the end of the condenser is noted and thereafter the cc. distilled noted at every even 10° C. continuing until 95 per cent. of the oil

has distilled. Toward the end, the condensing water must be heated to avoid separation of naphthaline.

C. Tar Acids.—The distillate from B is taken in the separatory funnel (Drawing 7, Fig. 3) as used in creosote oil and the tar acids determined in the same way.

D. Redistillation.—The extracted oil is placed in the Hempel apparatus (Drawing 8, Fig. 4 and 5) and redistilled, noting the cc. that have come over at 170° C. and 200° C., at which latter point the distillation is interrupted.¹

E. Napthalene.—The residue above 200° left in the flask in D is transferred to a copper beaker and cooled to 15.5° C. for fifteen minutes and the dry naphthalene determined as under creosote.

CARBOLIC OIL.

A. *Specific Gravity*.—Apparatus—see Drawing 8. If the oil is not limpid at 15.5° C., the gravity is taken at a higher temperature and 0.0008 added to the specific gravity for every degree above 15.5°.

B. Distillation—same as "Light Oil."

C. *Tar Acids*—same as "Light Oil."

BENZOLS.

A. *Distillation*.—Apparatus—see Drawing 8. Same as light oil, with the water in the condenser always cold.² With C. P. benzol or toluol readings are taken every 0.2° C.; with commercial benzols every 10° C. a reading is taken.

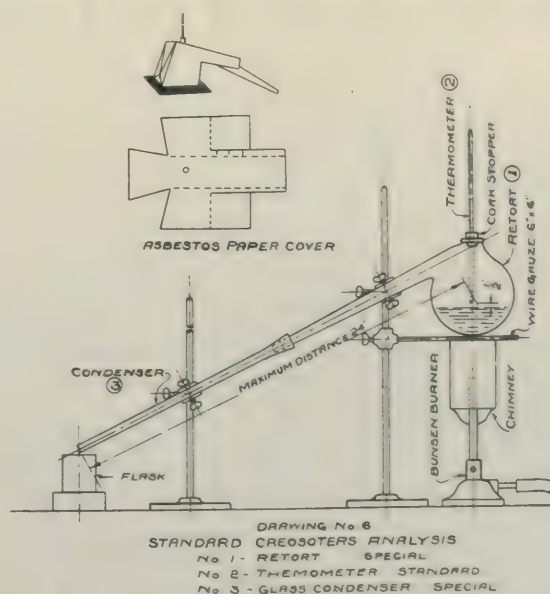
B. Gravity.—Hydrometer at 15.5° C.

C. *Wash Test*.—Taken only on water white grades.

About 7 cc. of concentrated H_2SO_4 and 21 cc. of the benzol are shaken in a small glass stoppered French square bottle of 30 cc. capacity and the coloration of the acid and oil noted.

CREOSOTE OILS.

A. *Standard Creosoters Distillation*.—Apparatus. Drawing 6. Method as given in *Bull.* 65, American



¹ The fraction -170°C. shows crude benzol, toluol and solvent; $170-200^{\circ}$ crude heavy naphtha.

² Distillation continued to dryness and drying point recorded.

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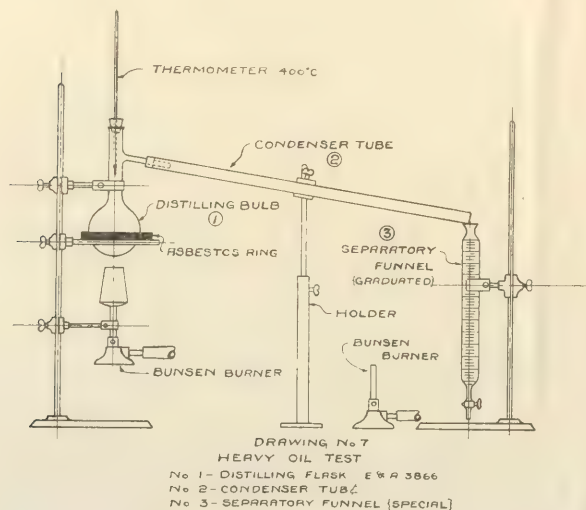
Before beginning the distillation, the retort should be carefully weighed and exactly 100 grams of the oil placed therein, the same being weighed in the retort. The thermometer should be inserted in the retort with the lower end of the bulb $\frac{1}{2}$ inch from the surface of the oil, and the condensing tube attached to

when the distillation should be recommenced, and the previous readings discarded.

In obtaining water-free oil, it will be desirable to free about 300 to 600 cc. of the oil by using the copper tar still and using 100 grams of the water-free oil for the final distillation. In the final report as to fractions, a correction must be made for the water content, so that the report may be made on the basis of a dry oil.

Determination of Specific Gravity of Oil.

In order to determine the specific gravity of any oil, heat the oil in a water bath until it is completely liquid. A glass stirring rod dipped into the liquid should show no solid particle on the rod when the same is withdrawn from the oil. When completely liquid, stir thoroughly and fill the hydrometer cylinder, which has previously been warmed. Insert a specific gravity hydrometer, taking care that the hydrometer does not touch the sides or bottom of the cylinder when the reading is taken. Take the temperature of the oil and make a correction for the specific gravity by reducing the same to the standard temperature of 15.5° C. or 60° F. The correct gravity is obtained by multiplying the correction figure 0.0008 by the number of degrees C., or



the retort by a tight cork joint. The distance between the bulb of the thermometer and the end of the condensing tube should not be less than 20 nor more than 24 inches, and during the progress of the distillation the thermometer must remain in the position originally placed.

The distillates should be collected in weighed bottles and all fractions determined by weight. Reports are to be made on the following fractions:

0 to 170 degrees Centigrade
170 to 200 degrees Centigrade
200 to 210 degrees Centigrade
210 to 235 degrees Centigrade
235 to 270 degrees Centigrade
270 to 315 degrees Centigrade
315 to 355 degrees Centigrade

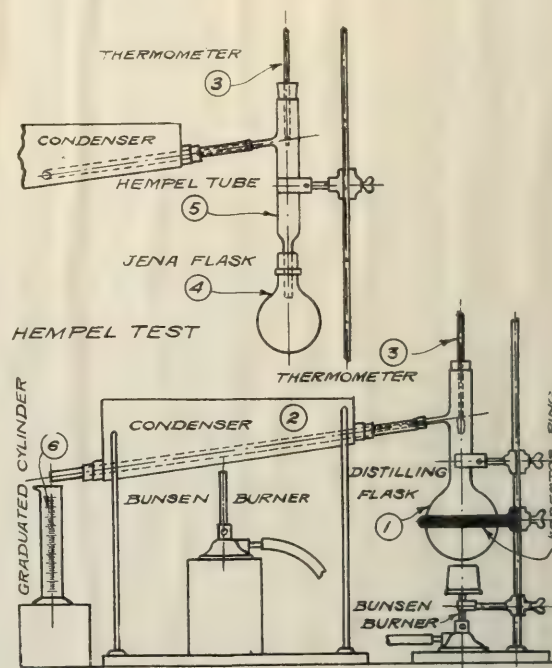
For practical purposes there will be no need of reporting on all of these fractions. It will be sufficient to report on the fractions as follows:

Below 200 degrees Centigrade
200 to 210 degrees Centigrade
210 to 235 degrees Centigrade
235 to 315 degrees Centigrade
Above 315 degrees Centigrade

Reports are to be made on individual fractions. In making such reports, it is to be distinctly understood that these fractions do not necessarily refer to individual compounds. In other words, the fractions between 210 and 235° will not necessarily be all naphthalene, but will probably contain a number of other compounds.

The distillation should be a continuous one and should take about forty-five minutes.

When any measurable quantity of water is present in the oil, the distillation should be stopped, the oil separated from the water, and returned to the retort



0.00044 by the number of degrees F., the oil is found to be above 15.5° C., or 60° F. and adding the product to the observed gravity.

NOTES.

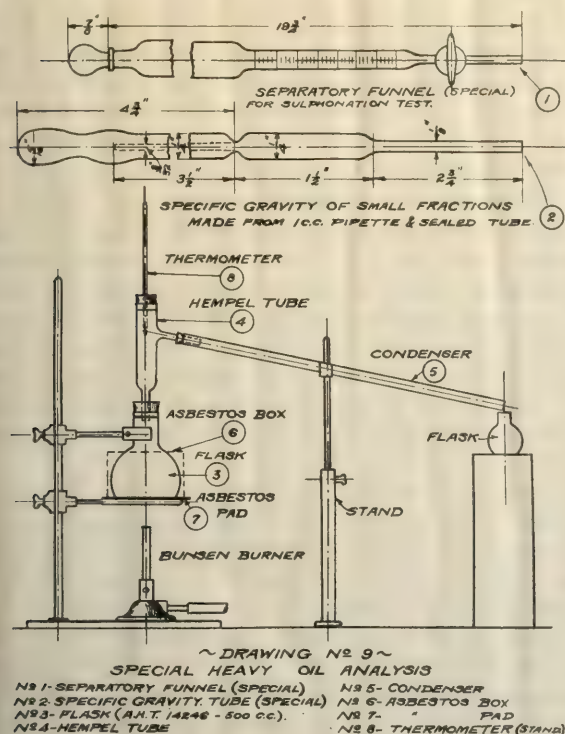
1. Emphasis is laid on attention to details and importance of a retort of the standard size.

2. The thermometer used must be of standard make, gas-filled and must be regularly tested for accuracy.

CREOSOTE OIL—ADDITIONAL TESTS.

A. *Drying Oil*.—Apparatus as in drying tar. 500 cc. are distilled up to 170°C ., the water noted and the oil distilling over returned to the still after cooling.

B. *Tar Acids*.—Apparatus shown in Drawing 7. 100 cc. of oil measured at limpid point, placed in Jena glass bulb and distilled. The distillation is continued until at least 95 per cent. has distilled off. The time from the first drop to the end should occupy about twenty minutes. The condenser tube should be kept warm enough by a flame during the operation to prevent distillate from solidifying. Warm the contents of the separatory funnel to 60°C . in water, and note



reading. Add 50 cc. of a 10 per cent. caustic soda solution. Shake well and allow to settle, drawing off the clear soda, warming again to 60° , and noting the shrinkage. Add 30 cc. of soda and note any further shrinkage. Repeat, if necessary, until no further shrinkage is noted. Then the total shrinkage is the per cent. of tar acids in the heavy oil.

C. *Dry Naphthalene*.—The extracted oil from B. is placed in a copper beaker and held at 15.5°C ., for fifteen minutes. The mass is filtered on a perforated funnel in a suction pump and sucked dry. The naphthalene in the filter is then pressed between paper in a letter press to remove all oil and weighed. The percentage is figured on the weights of original oil as given by the gravity at the limpid point.

D. *Limpid Point*.—About 5 cc. taken in a No. 4 or No. 5 test tube at 60°C . are cooled, stirring with a thermometer until the first crystals begin to form. This point is taken as the limpid point. Cool in water only, if necessary.

CREOSOTE OIL—SPECIAL TESTS.

A. *Distillation as in Circular 112, U. S. Department of Agriculture*, except that instead of the Hempel flask as described there, a 500 cc. Jena flask with a Hempel tube (shown in Fig. 3, Drawing 9) attached is used.

B. *Gravities*.—(Apparatus, Fig. 2, Drawing 9.) This is standardized with the pipette filled with water at 60°C . Oil at 60° is drawn up to the mark in the pipette, replaced in the outer tube and weighed. This can be used when only one or two cc. of oil are available.

C. *Sulphonation Test*.—Apparatus, Drawing 9. The weighed fraction distilling between 305° – 20°C . is warmed with concentrated H_2SO_4 (about 4–5 volumes) to 60°C . and the whole transferred to the separatory funnel (Fig. 1). The flask is rinsed three times with more concentrated H_2SO_4 and the rinsings added to the funnel. Then the funnel is stoppered and shaken, cautiously at first; afterwards vigorously, for about fifteen minutes. Then let settle over night. Then the acid is carefully drawn down into the graduated portion to within 2 cc. of where unsulphonated residue shows. Whether any is visible or not the test should be carried further as follows: Add about 20 cc. water and let settle for one-half hour. Then draw down water as close as possible without drawing out any supernatant oil or emulsion. Then add 10 cc. strong H_2SO_4 and let settle for fifteen to twenty minutes. Any unsulphonated residue will now settle out clear and give a distinct reading. If under 0.2 cc. it should be drawn down into the narrow part just above the stopcock where it can be estimated to 0.01 cc. The cc. are figured as percentages on the weight of the fraction taken.

If the unsulphonated oil is dark in color it should be treated with an excess of 10 per cent. sodium hydroxide solution. If the oil is soluble in this reagent, the test is regarded as negative.

THE BEHAVIOR OF HIGH-BOILING MINERAL OILS ON HEATING IN THE AIR.¹

By C. E. WATERS.

Received February 27, 1911.

HISTORICAL.

In a paper published some months ago, Schreiber² gives the results obtained when different cylinder and compressor oils were heated in a specially constructed air-bath through which a current of air, carbon dioxide or steam could be passed. The duration of the tests varied from 16 to 24 hours, and the temperature from 200° to 280° . The percentages of asphaltic material in the oil before and after heating were determined. The results showed that the amount of such material insoluble in benzene and in alcohol-ether greatly increased in the presence of air and of carbon dioxide, but was practically unchanged when the oil was heated in steam. Some of the oils became greatly thickened or covered with a surface skin, while others stood the tests remarkably well,

¹ Published by permission of the Director of the Bureau of Standards.

² *Z. angew. Chem.*, **23**, 99–103 (1910).

thus demonstrating their fitness for use in steam cylinders. A problem of a similar nature having been submitted to this Bureau, the present writer adopted, without knowledge of Schreiber's work, a method similar to his, but differing sufficiently from it in its details that the publication of this paper seems justifiable, especially as the oils to be tested were intended for use in gas engines. Without going immediately into details, it may be said that both Schreiber and the author heated to a considerably higher temperature than that adopted by most of the previous workers.

A summary of the more important work done along this line may not be out of place.

In 1884, Fox¹ investigated lubricating oils by a modification of a method described shortly before by Livache² for the recognition of drying oils. The oils were heated in sealed tubes with precipitated lead and the amount of oxygen absorbed was measured.

Zaloziński³ passed air through heated mineral oils and found acetic acid in the water formed by oxidation. The distillate had the odor of other members of the series of fatty acids. Engler and Bock,⁴ in addition to naphthenic acids, formed butyric and other fatty acids by blowing air through hot, neutral petroleum.

Charitschkow⁵ obtained two series of acid oxidation products, one from the alkali sludge, the other by oxidizing petroleum with air in the presence of alkali, at 150°. The latter series he later⁶ called "polynaphthene" or "asphaltogenic" acids.

In spite of conflicting statements,⁷ it is well established that mineral oils oxidize when raised to moderately elevated temperatures in the air. They may even oxidize at ordinary temperatures when exposed to sunlight, especially in the presence of alkalies. The writer has discussed this subject in another paper, in which it is shown that water and carbon dioxide are formed in addition to acids that remain in the oil.⁸

Another phenomenon closely connected with the formation of acids is the production of resinous or asphaltic substances when oils are heated in the air. This and the cracking of the oils are both probably concerned in the "carbonization" of gas engine cylinder oils. The cracking of mineral oils has, of course, been known for several decades, but a knowledge of the other chemical changes is not so widespread, although no argument is needed to convince one of its importance, especially to users of gas engines.

In 1894, Holde⁹ determined the asphalt content of certain dark-colored mineral lubricating oils before and after heating to 100° for 10 hours. He found that oils with little or no asphalt originally remained liquid; those with 1.3 to 2.3 per cent. became thick

and sticky; those with 5 to 6 per cent. were changed to a thick, resin-like mass. He showed later¹ that the gumming is due not only to a concentration of the asphalt as the oil evaporates, but also to a partial oxidation of the oil.

Adiasiewitsch² described the preparation of resinous products by blowing "deoxygenated air" through the residue in the petroleum still, the temperature varying from 150° to 200°. The resultant "resins" varied from thick liquids to solid, asphalt-like masses, and all were insoluble in petroleum distillates.

Mabery and Byerley³ also made asphalt from heavy petroleum residues by blowing air through the mass for four or five days, the temperature being kept at 650° F. Culmer⁴ obtained similar results in 40 hours at 193°.

In this connection may be mentioned the belief of Meyerheim,⁵ that the increase in the asphalt content with time is due to a polymerization of the oil or to a change of the asphalt from its original colloidal state to the insoluble form. Radium emanation caused no change in the amount.

Richardson and Hanson⁶ studied the change in viscosity of oils heated in thin layers at temperatures varying from 100° to 200°. In an atmosphere of superheated steam changes exactly similar to those in air were produced. Worrall and Southcombe,⁷ however, state that in cylinders heated as high as 750° F., steam causes no chemical change in the oil. The horny or granular deposit at times found in steam cylinders in Fe₂O₃ or Fe₃O₄ cemented together by oil.

Kissling⁸ determined the "resinification number" of oils. The amount of material precipitated by petroleum ether was determined after the oils had been heated at 125° to 135° for 12 hours on each of five successive days. The results show that less insoluble matter is formed in the better refined oils. The percentages of insoluble formed may vary a great deal more for different oils than the iodine and Maumené values. Kissling later⁹ published a somewhat modified method according to which the oil is treated with alcoholic soda, which extracts the "resin" originally present or formed by heating. The "coke-like" matter is thrown out by benzene. The oils are heated to 150° to 250°.

Letschford¹⁰ studied the oxidation of spindle oils when heated to 95° to 98° for 75 hours. The ratio of the product insoluble in petroleum ether to the original oil was called the "acid coefficient."

It is of fundamental importance to have a satisfactory method for determining the asphalt in oils. One method that has been tested is to determine the diminution in volume when the oil is shaken with

¹ *Z. anal. Chem.*, **23**, 434 (1884).

² *Mon. Sci.*, [3] **13**, 299; *Z. anal. Chem.*, **23**, 262 (1884).

³ *Z. angew. Chem.*, **1891**, 416-19.

⁴ *Cf. Chem.-Ztg.*, **16**, 592 (1892).

⁵ *Petroleum*, **2**, 480 (1907); *J. Soc. Chem. Ind.*, **26**, 402 (1907).

⁶ *Chem.-Ztg.*, **33**, 1165 (1909).

⁷ Hirsch, *Chem.-Ztg.*, **19**, 41 (1895).

⁸ *THIS JOURNAL*, **2**, 451 (1910).

⁹ *Mitth. kgl. tech. Versuchsanst.*, **11**, 261-72; *J. Soc. Chem. Ind.*, **13**, 668 (1894).

¹ *Mitth. kgl. tech. Versuchsanst.*, **13**, 174-96 (1895).

² See abstr. in *J. Soc. Chem. Ind.*, **15**, 346 (1896).

³ *Amer. Chem. J.*, **18**, 141-50 (1896).

⁴ *Rev. Prod. Chem.*, **2**, 356; *J. Soc. Chem. Ind.*, **19**, 525 (1900).

⁵ *Chem.-Ztg.*, **34**, 454 (1910).

⁶ *J. Soc. Chem. Ind.*, **24**, 315-19 (1905).

⁷ *Ibid.*, **27**, 308 (1908).

⁸ *Chem.-Ztg.*, **30**, 932-3 (1906).

⁹ *Ibid.*, **31**, 328 (1907); **32**, 938 (1908).

¹⁰ *Seifensiederz.*, **1908** No. 2; *Z. angew. Chem.*, **22**, 1066 (1909).

concentrated sulphuric acid and then allowed to stand. This has been found to be unreliable.¹

Distilling off the oil by means of superheated steam has also been recommended.² But practically the only method used is the precipitation by means of benzine or other light petroleum distillate. This is based on an observation by Bender.³ It has been found that the amount of insoluble matter precipitated depends on the boiling point limits of the benzine used. Hence the necessity for a carefully specified, "normal benzine."⁴ Still later, Kissling⁵ showed that benzines from different sources, though they may boil between the same limits, are not to be used indiscriminately if the results obtained by different chemists are to be compared. Thus, a sample of Kahlbaum's "normal benzine" gave lower values than benzine from Pennsylvania petroleum. Benzine from an Indian petroleum gave higher values than either of the preceding.

EXPERIMENTAL.

The four oils submitted to this Bureau had the following constants:

Sample.....	1	2	3	4
Flash-point.....	140°	224°	142°	142°
Engler no. at 50°.....	3.3	3.4	3.6	2.9
Engler no. at 100°.....	1.4	1.4	1.5	1.4
Acidity (percent. oleic acid)	0.033	0.024	0.023	0.025
Fatty oil.....	none	none	none	none

In the preliminary experiments, two mineral oils that had been on hand for a considerable time were used to test the method. Ten-gram samples were heated one at a time in matched Erlenmeyer flasks of 150 cc. capacity. The flasks rested on a small tripod of glass rod on the bottom of a large iron crucible, which was covered with a brass plate having a large hole through which the upper two-fifths of the flask projected. The bath was kept at 250° for one and one-half hours, and at the same time a fairly rapid current of air was passed in through a tube of Jena combustion glass bent at right angles at one end. Near the bend was a closely fitting sheath of brass tubing under which was a fish-tail burner for preheating the air. Concordant results could not be obtained on account of the impossibility of accurately regulating the two flames and the air current, all three varying from time to time during the day.

A cubical air-bath of sheet copper was then constructed. Openings were cut in the movable cover so that four flasks could be suspended by their necks. The sides and top of the bath were covered with sheet asbestos. A "rose" top was used on the burner, and the heating further equalized by means of a circular sheet of brass resting on a glass tripod about two centimeters high, on the bottom of the bath. The temperature was kept constant within two or

three degrees by means of a thermoregulator. There was nothing to prevent perfect freedom of diffusion of oil vapors and air at the mouths of the flasks.

Four ten-gram samples of the two trial oils were heated to 250° for three hours. The losses by evaporation did not agree very closely. To determine the amount of material insoluble in petroleum ether, 50 cc. of the solvent were placed in each flask, which was then corked, shaken gently and allowed to stand over night. The insoluble matter, except the coating on the walls of the flasks, was then filtered off in Gooch crucibles containing disks of S. & S. No. 589, blue ribbon filter paper covered with a thick felt of fine asbestos. The results are given in the table.

Sample.	A	A	A	A	B	B	B	B
Flask.....	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
Per cent. evaporation.....	5.00	4.50	6.20	7.90	9.44	7.35	9.29	15.92
Per cent. insol. filtered off....	0.55	0.48	0.51	0.55	0.34	0.42	0.40	0.37
Per cent. insol. in flask.....	0.10	0.25	0.15	0.05	0.09	0.37	0.39	0.08
Total insoluble	0.65	0.73	0.66	0.60	0.43	0.79	0.79	0.45

Duplicate tests were then made with the four samples of oil submitted to us for examination. The results follow.

Sample.	1	2	2	2	3	3	4	4
Flask.....	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
Per cent. evaporation.....	9.90	9.40	10.75	14.45	7.60	6.50	13.35	16.10
Per cent. insol. filtered off....	0.87	0.91	0.40	0.47	0.08	0.12	0.34	0.60
Per cent. insol. in flask.....	0.30	1.25	1.40	0.70	0.10	0.20	0.85	0.40
Total insoluble	1.17	2.16	1.80	1.17	0.18	0.32	1.69	1.00

An inspection of the results will show that the chief cause of the irregularities, when duplicates are run, is the insoluble matter remaining in the flask. This is a dark brown, varnish-like coating which does not dissolve in petroleum ether. Even when heated on the steam-bath for two or three days with chromic acid mixture, only part of it is removed, but soaking with alcoholic soda for two or three hours so loosens it that it may be rinsed out readily.

Duplicate determinations of the amount of flocculent matter filtered off agreed very well, except the results on No. 4. The flasks were not placed in the bath in any regular order, but in three of the heatings, flasks *a* and *d* gave low results on the coating or "varnish" (oils A, B, 1 and 2). This does not hold for oils 3 and 4, but even here, flask *a* showed less varnish than *b*, and flask *d* less than *c*.

It may be mentioned parenthetically that oil No. 3 was recommended by us as the best of the four. We have since learned that one of the other oils was first given a trial by the company for which the test was made. It proved to be entirely unsuitable, while No. 3, which was then used, has been satisfactory.

Variations in the condition of the walls of the flasks, all of which had been used for other purposes, seemed to be a possible explanation of the discrepancies in the amounts of "varnish" found. Accordingly, four new Jena flasks were carefully cleaned and used to obtain the following results. Only oil B was used.

¹ Aisinmann, *Dingl. Pol. J.*, **294**, 65-8 (1894); *J. Soc. Chem. Ind.*, **14**, 282 (1895). Charitschkow, *Petroleum*, **2**, 99-101 (1906); *J. Soc. Chem. Ind.*, **25**, 1140 (1906).

² Lecocq, *Bull. Soc. Chim. Belg.*, **22**, 81-7; *Chem. Abstr.*, **2**, 1880 (1908).

³ *Mith. kgl. tech. Versuchsanst.*, 311-16 (1890); *J. Soc. Chem. Ind.*, **10**, 354 (1891).

⁴ Holde, *Mith. kgl. Materialprüfungsamt*, **27**, 143 (1909).

⁵ *Chem.-Zig.*, **33**, 1203 (1909).

Flask.....	(a')	(b')	(c')	(d')
Per cent. evaporation.....	21.55	22.60	23.15	25.40
Per cent. insol. filtered off.....	0.32	0.32	0.44	0.61
Per cent. in flask.....	0.17	0.08	0.50	0.92
Total insoluble.....	0.49	0.40	0.94	1.53

A series of results was then obtained with a new set of flasks of "resistance" glass. Oil B was again used.

Flask.....	(a'')	(b'')	(c'')	(d'')
Per cent. evaporation.....	10.35	11.55	15.80	16.45
Per cent. insol. filtered off.....	0.33	0.44	0.25	0.23
Per cent. insol. in flask.....	0.45	0.82	0.29	0.11
Total insoluble.....	0.78	1.26	0.54	0.34

A consideration of all the figures obtained with oil B shows that while the "insoluble" filtered off varies from 0.23 to 0.61 per cent., nine of the twelve results lie within the limits 0.32 and 0.44 per cent. The average of these is $0.37\frac{1}{2}$ per cent., and the average of all twelve is $0.37\frac{1}{4}$ per cent.

Another interesting series of results was obtained by heating two lots of the oil B in resistance glass flasks. For the second heating the varnish was not removed, the flasks being thoroughly washed out with petroleum ether before a new lot of oil was introduced.

Flask.....	a	b	c	d
Per cent. varnish, first heat.....	0.11	0.30	1.20	0.48
Increase in varnish, second heat.....	0.82	1.94	1.03	0.46
Per cent. insoluble, first heat.....	0.26	0.30	0.55	0.32
Per cent. insoluble, second heat.....	0.50	0.40	0.57	0.64

It will be seen that the percentage of varnish formed at the second heat is higher than at first, except in flask *d*. The same is true of the insoluble matter precipitated from the oil.

It is unfortunate that Schreiber does not publish any duplicate determinations on the same oil, nor is he able, with his apparatus, to make any distinction between the "varnish" and the flocculent, insoluble matter. His statement that the formation of "asphalt" depends on oxidation, we can fully confirm, for in some of the earliest experiments we heated the oil in glass-stoppered bottles and found only traces of insoluble matter and no varnish at all.

In order to further test the possibility of variations being caused by the nature of the walls of the containing vessels, glass tubes of 20 mm. bore and 10.5 cm. long were made. Tubes of the same inside dimensions were made of ordinary brass, cold-rolled steel, and also from a steel containing 0.8 per cent. carbon, a vanadium steel, a chrome-vanadium steel and cast iron. These tubes were made in pairs. One of the vanadium steel tubes leaked so badly that it could not be used. Both of the cast iron tubes had fine pores through which a little oil escaped, but they became plugged up at the first heating. All of the tubes, except those of cold-rolled steel and brass, were made from the centers of the billets from which the standard samples issued from this Bureau were cut. Their size was necessarily limited and this had the disadvantage that only five grams of oil could be heated at a time, for when 25 cc. of ligroin were added after heating there was just enough space left to insert a cork safely. The metal tubes were

made with flaring, knife-edge rims to diminish creeping of the oil when the insoluble was filtered off.

In every case the oil, after dilution with petroleum ether, was allowed to stand about 22 hours, it having been found that the precipitate was less apt to clog the filter than when a shorter time elapsed.

For the heatings in the different tubes, three oils, designated as B, C and D, were used. They had been kept for a considerable time in closed tin cans. The organic acidity, saponification number and flash-point were determined.

Sample.	B	C	D
Organic acidity (as per cent. oleic acid)...	0.08	0.03	0.07
Fatty oil (approx.).....	none	none	0.5
Flash-point.....	205°	195°	195°

Oil B gave an incipient flash at 185°. The Pensky-Martens closed cup flash-point apparatus was used.

A complete series of heatings was run only with oil B, this having been considered unnecessary with C and D. The results are given below, expressed as percentages of insoluble matter and varnish.

GLASS TUBES.								
Oil.	B	B	B	B	C	C	D	D
Varnish.....	0.44	0.03	0.08	0.10	0.11	0.09	0.04	0.04
Insoluble.....	0.10	0.07	0.08	0.05	0.10	0.08	0.07	0.09

BRASS TUBES.								
Oil.	B	B	B	B	C	C	D	D
Varnish.....	0.02	0.03
Insoluble.....	0.15	0.18	0.15	0.16	0.13	0.15	0.07	0.06

CAST IRON TUBES.						
Oil.	B	B	C	C	D	D
Varnish.....	0.07	0.01	trace	trace	trace	trace
Insoluble.....	0.06	0.06	0.08	0.08	0.07	0.05

CHROME-VANADIUM STEEL TUBES						
Oil.	B	B	B	B	C	C
Varnish.....	0.05	0.04	0.03	0.02	trace	0.01
Insoluble.....	0.07	0.06	0.08	0.08	0.14	0.13

In the remaining tubes only oil B was heated.

Tube.	Vanad. steel.		Cold-rolled steel.			
Varnish.....	0.02	0.04	0.04	0.03	0.02	trace
Insoluble.....	0.07	0.08	0.08	0.08	0.09	0.09

0.8 carbon steel.				
Tube.				
Varnish.....	0.03	0.02	0.03	0.03
Insoluble.....	0.07	0.10	0.07	0.07

The above results seem to show that the material of which the tubes are made exerted an influence upon the amount both of the varnish and the precipitate formed in the oil itself. The differences are not great, but neither are the actual amounts large, most likely because of the relatively small surface of oil exposed to the action of the air. This area was only 3.14 sq. cm., while only double the amount of oil in a flask exposed a surface about nine times as great. The most striking discrepancy in the results is that oil D gave less insoluble in the brass tubes than in those of glass, while B and C yielded a much larger amount in the brass tubes. The reason for this may be that D contained approximately 0.5 per cent. of fatty oil, the others being straight mineral oils.

That the three oils show wider differences when heated in flasks is seen from the following figures

obtained with resistance glass flasks. The percentages of evaporation, varnish and insoluble are given.

Oil Flask	B (a)	B (b)	B (c)	B (d)	C (a)	C (b')
Evaporation....	19.00	19.03	19.95	15.08	17.15	25.75
Varnish.....	0.18	0.74	0.75	0.25	0.37	1.14
Insoluble.....	0.28	0.48	0.40	0.29	1.90	2.29

Oil Flask	C (c)	C (d)	D (a)	D (b')	D (c)	D (d)
Evaporation...	13.05	15.77	23.93	22.83	13.42	19.32
Varnish.....	0.38	0.43	1.01	0.57	1.27	1.25
Insoluble.....	1.88	1.81	2.30	1.89	2.25	2.50

Flask (b'), first used for oil C and subsequently for D, replaced (b) in which B was heated. It is curious that for one oil it gave high, and for the other low results.

In our opinion, the formation of "asphalt," or, as we have called it, "insoluble," is due to partial oxidation of the oil rather than to polymerization or to concentration of the asphalt as the oil evaporates. As mentioned above, there was practically no formation of insoluble when the oil was heated to 200° for three hours in stoppered bottles. When heated for the same length of time in flasks, loosely covered with watch-glasses, there was opportunity for atmospheric oxygen to enter as rapidly as it was absorbed by the oil. At the same time the lack of perfect freedom of diffusion allowed the escape of only the more volatile constituents so that the change in weight was negligible. No varnish was formed, but the following percentages of insoluble were obtained 0.47, 0.52, 0.38 and 0.33. Not enough of this oil was available for a test in the apparatus finally adopted.

Although the figures obtained by heating duplicate samples of the same oil side by side are often less concordant than could be desired yet, on the whole, the method seems to be capable of yielding data of value, this in spite of differences caused by unequal heating, variations in the rate of interdiffusion of oil vapors and air and, apparently, obscure catalytic phenomena influenced by the nature of the material in which the oil is heated. At present the method can be used to compare a limited number of oils with one another. To make it of perfectly general application would require a standard apparatus of carefully specified dimensions and material. The petroleum ether used would also need to be of very definite composition. Observing these and other obvious precautions, the requirements of the case would be more than met, for in actual practice the conditions must vary considerably more than in a laboratory experiment.

It is not claimed by any one who has worked along this line that the method does more than indicate what may be expected to happen when an oil is in actual use, but even a slight indication is of greater value than complete ignorance, and a laboratory test is more rational than placing implicit confidence in a dealer's statements.

It is our intention to go more fully into the question of standardization and also to study the effect of the

addition of fatty oils and other substances to the mineral oils before heating.

BUREAU OF STANDARDS,
February 22, 1911.

THE DETERMINATION OF MANGANESE BY THE SODIUM BISMUTHATE METHOD.¹

By PAUL H. M.-P. BRINTON.

Received December 24, 1910.

In looking over the tables of analyses furnished by the Bureau of Standards at Washington with its analyzed samples of steel, I noticed that the figures for manganese obtained by those chemists who used the sodium bismuthate method were in nearly all cases a little lower than the general averages obtained by all other methods. The differences were small, generally from 0.02 per cent. to 0.03 per cent., but as I had noticed the same thing in using the bismuthate method myself, I had a curiosity to learn the cause of this tendency of the process. I have made a little series of analyses and experiments, the results of which may be of some interest, especially to those who have not yet adopted the method in regular work.

As is well known, the method depends upon the oxidation of manganese to permanganic acid by adding solid sodium bismuthate to the cold nitric acid solution of the sample. The excess of the bismuthate is filtered off on asbestos, a measured excess of ferrous ammonium sulphate solution added to the filtrate and the latter then titrated back with potassium permanganate.

The method was originated by Schneider,² who used bismuth tetroxide, and subsequently developed by Reddrop and Ramage,³ and by Brearley and Ibbotson.⁴ Blair⁵ states that the sodium bismuthate method is not only remarkable in its simplicity and ease of manipulation, but that for samples containing not over 2 per cent. manganese it is the most accurate process known. The purpose of my work was to check up Blair's results (and those of the earlier workers also) and to confirm, if I could, his statement as to the accuracy of the method.

My analyses were made on various samples of the Bureau of Standards steels. I think we may take the averages given out by the Bureau, coming as they do from a variety of independent sources, as figures which represent the highest attainable accuracy in practical work. The methods and solutions were used, in the analysis of the steels, just as they are given by Blair. In the ferrous ammonium sulphate solution half the sulphuric acid was replaced by phosphoric acid, as suggested by Dr. C. B. Dudley. The end point is rendered a little sharper by this modification as the color due to the iron is less intense.

The solution of manganous sulphate for standardizing the permanganate was carefully analyzed,

¹ Read at the Minneapolis meeting of the American Chemical Society.

² *Dingl. Polytech.*, 269, 224.

³ *J. Chem. Soc.*, 67, 268; see also H. Ramage, *Chem. News*, 84, 209.

⁴ *Chem. News*, 82, 269; 84, 247.

⁵ *J. Am. Chem. Soc.*, 26, 793; also "Chem. Anal. of Iron," 7th Ed., 121, et seq.

the manganese being determined in weighed portions of the solution both as sulphate and as pyrophosphate. The results by these two methods were concordant.

The permanganate was standardized against the manganous sulphate solution, and also against pure Sørensen sodium oxalate, as well as against the "Sibley" standard iron ore issued by the Bureau of Standards. In standardizing against the ore, the iron was reduced with amalgamated zinc in a Jones reductor. The titer obtained by the sodium oxalate was identical with that by the standard ore.

Five of the standard steels were analyzed, the last one being a vanadium steel. Table I shows a comparison between the results obtained by taking the strength of the permanganate as determined by the manganous sulphate method, and by taking it as determined by sodium oxalate or by the "Sibley" ore. In these determinations the theoretical conversion factors were used: $\text{Na}_2\text{C}_2\text{O}_4$ to Mn 0.16024, and Fe to Mn 0.1967.

TABLE I.

	Per cent. manganese.				
Bureau of Standards averages	0.412	0.916	0.760	0.568	0.669
Found with MnSO_4 as primary standard.....	0.410	0.922	0.757	0.557	0.663
Found with $\text{Na}_2\text{C}_2\text{O}_4$ or with iron ore as primary standard	0.411	0.920	0.758	0.562	0.665
	0.397	0.892	0.732	0.539	0.642
	0.398	0.890	0.733	0.544	0.644

From these figures it is seen that the results come somewhat low if the permanganate is standardized against sodium oxalate or against an iron compound, and the theoretical conversion factor used. It is interesting to note that the results in this table obtained by the latter method agree very closely with those obtained by the analysts who used the sodium bismuthate method in the analyses published by the Bureau of Standards with these samples. (The vanadium steel is an exception.)

The results obtained by standardizing the permanganate against the manganous sulphate solution are highly satisfactory, and a great many determinations which I have made in addition to those given in the table have convinced me that the degree of accuracy there shown can be regularly attained; and the process is so simple that no unusual manipulative dexterity is required to insure correct analyses. In fact it is hard to go wrong with the methods, after the correct titer for the permanganate is once obtained.

While standardizing against a weighed quantity of manganous sulphate solution is the most accurate method known for the purpose here desired, it is also the most tedious. It requires a gravimetric determination of the manganese in the solution, and upon this result depends the accuracy of the whole process. A slight error made at this point introduces serious discrepancies in the final results.

The simplest method of standardizing is against pure sodium oxalate; but since the figure obtained in this way brings the results too low we must use an empirical factor. The ratio $5\text{Na}_2\text{C}_2\text{O}_4 : 2\text{Mn}$ calls for the figure 0.16024, but to obtain correct results I find that the factor 0.1656 must be applied.

Since permanganic acid has a certain tendency to decompose in dilute nitric acid solution, particularly in the presence of much ferric nitrate, it was deemed advisable to investigate the rate of decomposition. Referring to the solution after the excess of bismuthate has been filtered off and when it is ready to receive the ferrous ammonium sulphate and be titrated back with permanganate, Blair¹ says: "At a temperature of 5° C. the solution will remain unaltered for several hours, but at 40° C. fifteen minutes will show an appreciable change." The temperature of a laboratory is never so low as 5°, nor so high as 40°, so to see what danger from this decomposition would be if artificial cooling were not resorted to, I made the following series of determinations on the 0.760 per cent. manganese steel from the Bureau of Standards. The temperature of room and solutions was 21° C.

TABLE II.

	Found. Per cent. Mn.
1 Run strictly according to Blair. The filtration took about 4 minutes, and the ferrous ammonium sulphate was added and excess titrated immediately.....	0.760
2 Process same as before, except that after filtering, an interval of 12 minutes was allowed before adding ferrous ammonium sulphate and titrating.....	0.758
3 Same, but an interval of 25 minutes was allowed.....	0.755
4 Same, but an interval of 55 minutes was allowed.....	0.750
5 Same, with an interval of 1 hour and 30 minutes.....	0.740

From these figures it appears that a delay of ten or fifteen minutes is practically without effect under ordinary conditions. Twenty-five minutes causes a slight lowering of the results, and a longer time than this has a decidedly unfavorable influence.

It may be mentioned in passing that a large excess of bismuthate is inadvisable, since it not only increases the cost of the process, but also tends to clog the filter rapidly so that fewer filtrations can be made on the same asbestos felt. Just enough bismuthate should be used so that a slight excess is plainly visible in the bottom of the flask or beaker.

As regards the application of the method to iron ores low in manganese, I find the method advised by Blair, *i. e.*, treatment of the sample with 10 cc. water, 4 cc. H_2SO_4 and 10-20 cc. HF in a platinum dish or crucible, somewhat tedious; and that it requires so large an amount of platinum if many samples are to be run is a further disadvantage. I prefer to dissolve the ore, about 1 gram, in 12 cc. of concentrated hydrochloric acid in a 4-oz. Erlenmeyer flask, evaporate almost to pastiness, and then add 4 cc. of concentrated sulphuric acid. By boiling down to heavy fumes over a free flame, manipulating the flask in a holder, the hydrochloric acid is so completely expelled that no test for chlorides can be obtained with silver nitrate. The residue is then taken up with 50 cc. of nitric acid, sp. gr. 1.135, and finished as usual. The process is quite rapid and the results very accurate. A few ores will not yield all their manganese to this treatment, so if the residue appears dark after taking up with nitric acid, it should be filtered off, fused with a very small amount of potassium bisulphate and added to the main por-

¹ Loc. cit.

tion. It should be noted that this same treatment of the residue may be necessary with some ores even when using the hydrofluoric method of attack. The fact that the method as above given does not eliminate the silica is not really a drawback, since the silica is obtained in a form which does not seem to clog the filter much.

Attacking the ore by fusing with sodium peroxide was also tried and it proved fairly successful. Were it possible to procure iron crucibles free from manganese this would be the ideal method. Since that seems to be impossible at present, I had to use nickel crucibles. It should be noted that some nickel contains traces of manganese, but not, I believe, as a rule. In using this method, 1 gram of ore is fused with about six grams of sodium peroxide at as low a heat as possible. A minute or two in liquid fusion is all that is necessary. The crucible and contents are treated with water in a covered beaker, and when the action is over the crucible is removed and one-third the volume of concentrated nitric acid added. The solution is boiled until all hydrogen peroxide is decomposed and everything dissolved but some manganese dioxide which has been precipitated. Ferrous sulphate is added until the manganese is reduced, the lower oxides of nitrogen are boiled off, and the analysis is finished as usual. The crucible is considerably attacked, but if the heat is kept low a dozen fusions may be made in a crucible before it is unfitted for further use. The color, due to the nickel, tends to obscure the end point with permanganate somewhat, but after a little practice the point can be readily seen.

SUMMARY.

1. Corroboration of Blair's statement that for small amounts of manganese the bismuthate is the most accurate method known.

2. When the potassium permanganate is standardized against sodium oxalate or iron, and the titer theoretically calculated, the results come out too low. A gravimetrically standardized manganous sulphate solution is the correct primary standard, but as this method is more inconvenient than the sodium oxalate method, it is suggested that pure Sørensen sodium oxalate be used, and that the empirical factor 0.1656, and *not* the theoretical factor 0.16024, be used in the conversion of the sodium oxalate figure to that for manganese.

3. The decomposition of ores by the hydrochloric and sulphuric acids method is suggested as being fully as accurate, more rapid and perhaps more convenient than the hydrofluoric and sulphuric acids method. Fusing the ore with sodium peroxide is recommended as a method suitable for refractory ores.

UNIVERSITY OF MINNESOTA.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF APPLIED CHEMISTRY,
MASS. INST. OF TECH.]

METHOD FOR TESTING GALVANIZED IRON TO REPLACE THE PREECE TEST.

By WALTER A. PATRICK AND WILLIAM H. WALKER.

Received February 27, 1911.

Some time ago one of us¹ published a paper on the testing of galvanized and other zinc-coated iron, in which it was shown that the so-called Preece Test was unsatisfactory from many points of view, although no alternative method was shown to be equally available. This study has been continued, and it is now believed that a satisfactory substitute can be given.

The Preece Test consists in placing the piece of galvanized iron to be tested, in a solution of copper sulphate under standard conditions, and observing the number of one-minute immersions which can be made before copper in a bright adherent form will plate out on the article. The accuracy of the test depends upon the following assumptions: first, that the zinc will pass into solution and be replaced by copper at a definite rate, and hence the *time* taken to dissolve a galvanized coating will measure its thickness; second, that the galvanized coating is homogeneous and that the speed of the reaction between the coating and copper sulphate is constant, that is, the rate of solution is uniform; third, that when the iron base is reached the copper will plate out on the iron in a bright adherent film, in contradistinction to the black spongy form in which it appears upon the zinc coating, and that no bright copper will be seen until the iron base is thus uncovered.

STRUCTURE OF ZINC COATING.

The correctness of the first two assumptions depends upon a homogeneous structure of the galvanized coating. Although a detailed description of the structure of the different forms of zinc-protected iron now on the market will form the subject of a later paper, we will point out at this time that this structure is such as would almost certainly preclude the possibility of the Preece Test being a valid one.

The coating of an ordinary hot dipped sheet or wire is made up of three well defined parts, namely, the iron base or foundation upon which the coating rests, then a layer of an iron-zinc alloy, and next to this the layer of zinc. The thickness of the alloy depends upon the temperature of the galvanizing bath, the length of time the iron is in contact with the molten zinc, and upon the flux which is used. In a previous paper, one of us² stated that this layer of alloy was electro-negative to the iron. This was an error introduced by the use of measurements of absolute potential, and which we herewith desire to correct. The alloy is much less electro-positive than zinc, but is not electro-negative. Since the rapidity with which the zinc or zinc alloy will pass into solution, and an equivalent weight of copper be precipitated in its place, is a function of the difference of potential between the two metals, it will be

¹ Walker, *Proc. Am. Soc. Testing Materials*, 9, 431.

² *Loc. cit.*, p. 432.

seen that the rate of solution must of necessity change as we pass from the zinc to the alloy. The so-called sherardized iron and some kinds of electro-galvanized iron consist so largely of an iron-zinc alloy that any test or measurement based upon an assumed uniformity in rate of solution is liable to grave error and untrustworthy.

SPEED OF SOLUTION.

[When a piece of clean zinc is placed in a reasonably concentrated solution of copper sulphate, the rate at which zinc will pass into solution and an equal number of copper ions be precipitated as metallic copper will depend upon the concentration of the copper ions in the solution in the immediate vicinity of the metallic zinc. If for any reason the solution become depleted in copper ions, the speed of this interaction will decrease. This is just the condition which obtains when a one-minute immersion is used in the Preece Test. For the first few seconds the reaction is very rapid, but as the spongy copper forms on the surface of the zinc it becomes more difficult for the zinc ions formed to get away, and fresh copper ions to reach the metallic zinc, so that at the end of a minute the reaction has practically ceased. When the sponge of precipitated copper is removed and the test piece replaced in the solution action again begins vigorously but again falls off. It can easily happen, therefore, that the iron base will be practically exposed at, say, the end of the second minute, and yet no bright copper will be seen until the sponge is removed at the end of the third minute. The test will thus be classed as a three-dip piece, while in reality it is but a trifle over two-dip, and an error of 33 per cent. is thus introduced. In fact, we have seen galvanized iron which showed areas of *no coating* whatever. The Preece Test would indicate such wire as one dip when in reality it was zero-dip wire.

APPEARANCE OF BRIGHT COPPER.

It has been proposed to provide against the above difficulty by using a number of ten-second immersions instead of one-minute immersions. But a new difficulty here arises. As is well known, when a piece of iron is placed in a neutral copper sulphate solution iron passes into solution and copper plates out in a bright adherent film. The appearance of this bright copper is taken in the Preece Test as an end point, and as a proof that the zinc has all been dissolved and the iron base exposed. The fundamental error here introduced can be easily shown by immersing a piece of smooth spelter or sheet zinc to a number of ten-second immersions in the Preece copper sulphate solution. In a short time a point of bright copper will appear which as the test proceeds will spread over the entire surface, and were the specimen being tested a galvanized article instead of one of pure zinc, the totally erroneous conclusion would be reached that the iron base had been uncovered, and the test concluded. This layer of bright copper is formed more easily on the zinc-iron alloy than it is upon pure zinc. Care must be taken, therefore, in carrying on the Preece Test to avoid conditions

which would subject the test specimen to a dilute copper sulphate solution, such as obtains when the specimen is frequently rinsed with water, and to avoid a burnishing or rubbing action when the specimen is cleaned.

We attempted to show the change in rate of solution as we passed from the zinc layer, to the zinc-alloy layer, by plotting the loss in weight of coating against the time of immersion. Owing to this irregular tendency of the copper to remain attached to the coating and to more or less protect the coating underneath from solution, the results were altogether misleading. Although this abnormal appearance of bright copper is much less liable to occur when one-minute immersions are employed, no dependence can be placed upon the end point as thus obtained.

CAUSTIC SODA METHOD FOR TESTING COATING.

We have already pointed out that hot concentrated caustic soda will dissolve the zinc coating when placed in contact with iron. Under some conditions an alloy very high in iron is left upon the iron base. Altogether the method is not a convenient or a rapid one, and therefore we desire to propose the following substitution for the Preece Test, devised by Mr. Patrick.

BASIC LEAD ACETATE METHOD.

When a zinc-coated iron article, free from the products of corrosion, is placed in a basic lead acetate solution at ordinary temperature, the coating passes into solution and an equivalent amount of metallic lead is precipitated in a loosely adherent form upon the specimen. This lead is easily removed and the coating determined by measuring either the loss in weight of the test specimen, or the lead precipitated. The reaction is retarded by the precipitation of the lead and therefore when a heavily galvanized piece is being tested this lead must be periodically removed. Either a volumetric or a gravimetric method for determining the coating may be employed, according to whether a balance is available or not. If the volumetric method is used, this lead must be preserved, while if the specimen be weighed the lead may be discarded, unless on account of the size of the specimen it is found desirable to collect and weigh the lead. When the iron-zinc alloy is thus dissolved, the iron of the alloy passes into solution, and existing as basic iron acetate colors the solution red as it oxidizes. If desirable this iron can be determined by weighing as oxide, or by titration with standard oxidizing solution. When the coating has all been removed and bright iron only is visible, either the lead is quantitatively determined, or the iron base is dried and reweighed.

SAMPLE.

The size of sample must of necessity depend upon the material under investigation. In the case of sheets or plates, a piece 2 by 2 inches, and for wire a piece 3 to 6 inches is desirable, according to the gauge. The size of the wire and sheet should not vary more than $\frac{1}{64}$ inch plus or minus. The longer the test piece, the smaller is the percentage error

of measuring. The specimen should be weighed if the gravimetric method described below is to be employed, to three decimal places if possible.

SOLUTION.

The solution should be made up as follows: 400 grams of crystallized lead acetate are dissolved in one liter of water and four grams of finely powdered litharge added. The mixture is shaken until most of the litharge is dissolved. Any insoluble residue may be allowed to settle to the bottom from which the clear solution is later decanted and diluted to a specific gravity of 1.275 at 15.5° C. This produces a solution of basic lead acetate which dissolves zinc and zinc-iron alloy but does not attack the iron base.

METHOD OF IMMERSING.

Enough of the lead acetate solution should be employed to completely cover the specimen, and, on the other hand, the specimen should be so placed in the containing vessel that the zinc surface is completely exposed to the solution. This is a matter of detail that will vary with the form of the specimen, but wire should be placed on end and sheets on an edge, in order that the zinc acetate formed may readily pass off into solution. Tall, narrow, glass cylinders are desirable for the wire, while beakers or thin glass water tumblers may be used for sheets or other forms.

TIME OF IMMERSION.

The test specimens should be allowed to remain in contact with the solution for three minutes. The adherent lead is then removed from the specimen with the hands, a rubber "policeman," or a stiff brush (into preferably another beaker or tumbler, if the lead is to be determined). A burnishing action must be avoided as under some circumstances closely adherent lead may be plated out on the zinc. The specimen is then replaced in the lead acetate solution and after another three-minute immersion the lead is again removed as before. This is repeated until the bright surface of iron is exposed. Four three-minute immersions are usually sufficient. The bright iron base differs so radically in appearance from both the spongy lead, or even lead in the form of a bright adherent film, that a *lack of uniformity* in the thickness of the coating is readily detected. This is an important point in testing wire. A thin place on the wire may frequently show the bright iron surface after the first immersion; we have found some specimens of galvanized wire which over considerable areas carried no coating at all. On such places no lead is precipitated, and the bare iron easily recognized.

DETERMINATION OF COATING.

(A) If a balance be employed the bright iron piece is now thoroughly washed with water, rinsed in alcohol, and dried and weighed. The difference between the first and second weighings gives the weight of coating on specimen employed. Suitable factors for converting this into weight per unit area are given later; but, for example, if exactly 6 inches

of wire be used, the weight of coating in grams as above determined, multiplied by 23.31, gives the weight of coating in pounds per mile of wire. This value can be readily calculated into pounds of coating per ton of wire if the weight of the wire per foot be known. If the weight of the test specimen be very large with respect to the weight of the coating, small errors in weighing invalidate the accuracy of the test. In this case it is best to collect the lead either on a Gooch crucible, and wash with boiled water and weigh, or to gather it together into a lump and weigh after washing with boiled water by decantation.

(B) If no balance be available the weight of zinc per mile or per unit area can be determined volumetrically as follows: the accumulated lead from the specimen is washed by decantation several times with hot water previously boiled, until free from lead acetate. This is very readily accomplished. The metallic lead is dissolved in a small quantity of hot concentrated nitric acid, for example, two cubic centimeters. This solution is then neutralized with a slight excess of ammonia and without filtration re-dissolved in acetic acid. A standard solution of potassium chromate (K_2CrO_4) is prepared containing exactly 12.624 grams per liter. Potassium chromate reacts with lead acetate, giving yellow lead chromate. On the other hand, silver chromate is deep red. So long as there is any lead acetate in the solution, the potassium chromate will unite with this lead acetate, so that if a little of this solution be placed on a paper containing silver nitrate no reaction will be observed. The moment enough potassium chromate is added to entirely precipitate the lead, the first drop of excess of potassium chromate will color silver nitrate paper red and thus determine the end-point of the reaction. By measuring from a burette, therefore, the exact number of cubic centimeters necessary to give the first indication of red with silver nitrate paper and using the following factors, the weight of zinc per unit area can be directly computed.

FOR WIRE.

Length of test piece taken in inches.	Factor for converting cubic centimeters into lbs. coating per mile.
1.....	0.60
2.....	0.30
3.....	0.20
4.....	0.15

FOR SHEETS.

Size of test specimen.	Factor for converting cubic centimeters into ounces coating per square foot.
1 sq. inch.....	0.0213
4 sq. inch.....	0.0053

It is apparent that working charts may easily be prepared from which the data desired can be read off directly. The following formulae express the relationships most frequently used:

- Let X = pounds coating per mile of wire.
- Let Y = ounces coating per square foot of sheet.
- Let N = cubic centimeters potassium chromate solution used.
- Let L = length of test piece in inches.
- Let S = area of test piece in square inches.
- Let G = loss in weight in grams.

$$X = \frac{139.86 \times G}{L}$$

$$= \frac{0.60 \times N}{L}$$

$$Y = \frac{5.090 \times G}{S}$$

$$= \frac{0.0213 \times N}{S}$$

The manufacturers of both sheets and wire publish small handbooks which may be had for the asking, giving the gauge, relation of weight to area and length and other data for further calculations.

The following results obtained by this method on three samples of No. 9 gauge wire are fairly representative of the accuracy attainable:

LENGTH OF TEST SPECIMENS, THREE INCHES.

Sample No. 1.	Loss of weight.	Lbs. coating per mile of wire.	Lbs. coating per ton of wire.
Analysis 1....	0.1030	4.81	31.07
Analysis 2....	0.1010	4.75	30.68
Analysis 3....	0.1025	4.79	30.94
Analysis 4....	0.1035	4.86	31.39

Sample No. 2.	Loss in weight.	cc. K_2CrO_4 used.	Lbs. coating per mile of wire.	Lbs. coating per ton of wire.
Analysis 1....	0.1845	8.55	55.23
Analysis 2....	42.7	8.54	55.17
Analysis 3....	42.6	8.52	55.04
Analysis 4....	42.8	8.56	55.29

Sample No. 3.	Loss in weight.	cc. K_2CrO_4 used.	Lbs. coating per mile of wire.	Lbs. coating per ton of wire.
Analysis 1....	0.1050	4.93	31.85
Analysis 2....	24.8	4.96	32.04
Analysis 3....	24.6	4.92	31.78
Analysis 4....	24.7	4.94	31.91

DETERMINATION OF IRON IN ALLOY OF COATING.

The iron which is in combination with zinc in the coating as an iron-zinc alloy will pass into solution as iron acetate and can be determined as follows: the combined lead acetate employed for the sample, together with the wash waters from the metallic lead, is heated to boiling and the lead precipitated with a slight excess of sulphuric acid, the iron oxidized with nitric acid, and precipitated with ammonia, washed and weighed as iron oxide. Or if no balance be available, it may be washed, re-dissolved in sulphuric acid, reduced with zinc, and titrated with standard potassium permanganate solution. An idea of the amount of iron in the different kinds of zinc-coated iron may be obtained by the following results obtained from products found in the open market.

Kind of material.	Iron in coating. Per cent.
Ordinary hot dipped sheet.....	2.26
Sherardized plate.....	11.70
Wet galvanized (electro deposited) sheet.....	trace
Wet galvanized (electro deposited) sheet.....	7.46

NOTES.

(1) In order to insure the absence of free acetic acid, and to eliminate any danger of the iron base being attacked, enough lead oxide is added to render the resultant solution slightly basic.

(2) It is important to immerse the test specimen for periods not shorter than three minutes at a time. Otherwise a coherent deposit of lead may be formed.

(3) In the case of articles that are weathered, or have been subjected to corrosion, it is necessary first to remove the layer of zinc salts from the surface by immersion in dilute hydrochloric acid. In such cases the gravimetric determination by difference must needs be used to obtain accurate results.

(4) In washing the metallic lead free from lead acetate, it is necessary in very accurate work to use water previously boiled to free it from oxygen and carbon dioxide.

(5) In order to obtain exact lengths of wire, it is well to cut the specimen a little longer than desired and file to exact measurement.

(6) The presence of a deep red color in the lead acetate after a test must not be taken as indicating a large amount of iron. Traces of iron as basic ferric acetate produce a strong color.

(7) If the iron is determined by titration with potassium permanganate, it is necessary to first remove it from the acetic acid, as with acetic acid potassium permanganate titration is not accurate.

(8) The size of the specimen which can be taken, if the volumetric method be used, is limited by the amount of potassium chromate solution required for reacting with the precipitated lead. Three inches of wire are all that are necessary, except that greater accuracy in measuring is obtained by using a longer piece.

(9) Even when employed in the same way in which the Preece Test is used, the lead acetate solution has important advantages over copper sulphate in this: that a bright copper surface on the zinc cannot be distinguished from the bright surface on the iron base. In the lead acetate solution, bright adherent lead may be precipitated, but cannot be mistaken for the bright iron. Hence, if it is desired to make a rough test for uniformity of coating on a wire, one-minute dips may be employed, and the uniformity with which the bright iron appears indicates the evenness of the coating.

THE FORMATION TEMPERATURE OF CARBORUNDUM.

By HORACE W. GILLET.

Received March 1, 1911.

The temperature at which carborundum is formed has been given in the literature at values varying from 1200° C. to 3870° C.¹

The only values on which any degree of dependence can be placed are those of Tucker and Lampen² who give for the formation of carborundum 1950°, and of graphite from carborundum, 2220° C. Some experiments having indicated that carborundum was formed at a lower temperature led to an investigation of the point.

The furnace used in the final runs was about 27

¹ Stansfield, *The Electric Furnace*, 1907, 152; Acheson, *Electrochem. Ind.*, **1**, 332 (1903); U. S. Pat., 723,631; Dunlap, *Electrical Review*, **53**, 702 (1903); Scott, *Jahrbuch d. Electrochemie*, **12**, [2] 734 (1903); *J. Soc. Chem. Ind.*, **24**, 501 (1903); *Proc. Faraday Soc.*, April 4, 1905; Kunz, *Trans. Am. Electrochem. Soc.*, **7**, 249 (1905); Pring, *J. Chem. Soc.*, **93**, 2104 (1908); Greenwood, *Ibid.*, **93**, 1483 (1908); Pring and Fielding, *Ibid.*, **95**, 1501 (1909); *Dict. Chem. Met. Material*, 1909, 19; Tucker and Lampen, *J. Am. Chem. Soc.*, **28**, 853 (1906).

² *Loc. cit.*

inches long and 16 inches in diameter, being built up of fire brick in about the shape of the present commercial furnace.¹ This held about 150 lbs. of charge and took up to 50 K. W. The electrodes were usually of 2" × 4" carbon and were held in water-cooled holders. The core was 2 inches wide, 4 inches high, and 16 inches long—of crushed carbon, 98 per cent. of which was between 4 and 12 mesh. The charge was 53.5 parts quartz sand, 40.0 of 14-mesh coke, 5.0 sawdust and 1.5 NaCl, which is practically the composition of the commercial charge.²

The temperatures were measured either by a Wanner pyrometer with special dark glass, a Morse or a Thwing radiation instrument made especially for our purposes. The calibration of these for a range of 1500°–2500° C. was a problem in itself and had to be worked out independently, since the Bureau of Standards has not taken up the work of calibration at these temperatures. They were calibrated against a black body whose temperature was measured by a Bureau of Standards thermocouple through its range, and above that on the basis of Wien's Law for the optical instruments, using a spectrophotometer, and of the Stefan-Boltzman Law for the radiation instrument. An account of the calibration will be found in the *Journal of Physical Chemistry* for March, 1911.³ The degree of accuracy obtained was about 10° C. at 2500°.

The greatest difficulty in high temperature measurements in the electric furnace is the fumes evolved,⁴ which either interfere with or entirely vitiate the readings made with optical and radiation pyrometers.

A tube was devised which solved the fume problem for our laboratory conditions and which might perhaps be used even in commercial work. This is shown in Fig. 1.

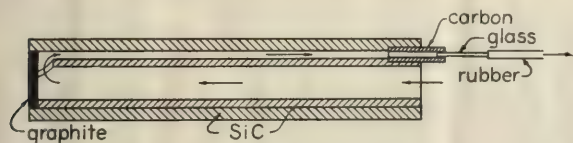


Fig. 1.—Temperature tube.

On the scale we were working the outer tube was 2½ inches O. D., 1¾ inches I. D., 12 inches to 18 inches long, closed at one end by a graphite plug 3/16 inch thick, with a matt surfaced face, and so ground as to insure a tight fit. The inner tube was 1½ inches O. D., 1 inch I. D., 12 inches to 18 inches long—placed close up against the plug, a notch being cut in the end to allow air to pass freely. A small carbon tube 4 inches long was fitted between the two main tubes, the joint between outer and inner tubes being packed with fibrous asbestos and all joints luted tight with a paste of 3F carborundum and water glass.

A glass tube was fitted into the carbon tube and gentle suction from a Chapman pump applied through

a rubber or flexible metallic tube. The course of the air is shown by the arrows in the figure. The current of air effectually removes the fumes and makes temperature observations easy. The 3/16 inch graphite plugs would last through a six-hour run at temperatures of 2300°–2500°.

The air is preheated before striking the plug, and cooled off on its outward journey; this cuts down the cooling effect we expected the air current to have to such a degree that no measurable difference in the readings was detected whether the air current was fast or slow or, in the rare cases where the fumes did not interfere, off entirely.

The temperature drop through the 3/16-inch plug was found to be about 25° at 1800°, falling to 15° at 2500° C. for our furnace. A correction of +20° added to the readings on the front of the plug would be close enough to give the temperature at the back through this range, for our conditions, though the exact values from 1350° up were determined and used.

The question whether or not the plug in this form of tube gave true black body radiation was very carefully investigated by the use of a spectrophotometer, on the basis of Wien's Law,¹ and no detectable deviation from complete black body radiation could be discovered.

In deciding on the material for the main tubes in the device for overcoming fumes, we were influenced by a desire to have the temperature gradient through the tube as nearly as possible the same as through the furnace itself. Graphite tubes are easily worked, but the heat conductivity of graphite is much greater than that of carborundum or siloxicon. Carbon tubes have less heat conductivity than graphite, but still more than carborundum. What we wanted was a material that would have approximately the thermal conductivity of the charge in the outer zone, that of siloxicon in the siloxicon zone, of SiC in that zone and of graphite in its zone. Also as the zones widen out the tube should change with them. All this is manifestly impossible, but a close approximation was made by having the National Carbon Co. make up tubes of carborundum composition. These tubes contained from 70 per cent. to 80 per cent. of fairly finely ground SiC, the rest being mainly carbon, either put in as such or derived from the binder used. They gave an apparent density of 2.22 against 1.53 for the usual carbon tube. They were less permeable to gases than carbon tubes, and showed a crushing and transverse strength approximately the same as carbon.

These tubes would be expected to give pretty close to the furnace gradient in the carborundum zone, and since the SiC in the tube was always found to be decomposed to graphite in the part projecting into the graphite zone, the gradient through these two most important zones is closely that of the furnace.

To test this, a run was made with three tubes, one each of graphite, carbon and carborundum. The core for this furnace was made with great attention to uniformity of cross section, so as to insure uniformity of heating. The tubes were equally spaced along the

¹ See *El. Met. Ind.* **7**, 190 (1909).

² Tone, *Met. Chem. Eng.*, **8**, 148 (1910); U. S. Pat., 949,386.

³ Gillett, "Temperature Measurements in an Experimental Carborundum Furnace," *J. Phys. Chem.*, **15**, 213 (1911).

⁴ Burgess, *Trans. Am. Electrochem. Soc.*, **11**, 257 (1907).

¹ Gillett, *loc. cit.*

middle of the core, the middle point of the $2\frac{1}{2}$ inches in diameter tube being in each case 4 inches from the middle point of the next tube.

Previous experiments had shown that the cooling effect of the electrodes did not extend far enough into the furnace to affect the core temperature over the space in which the tubes were placed. Each tube projected 1 inch into the open air, through the fire brick walls. The graphite tube was placed in the center and the others on each side.

Between the graphite and SiC tubes and exactly 3 inches back from the nearer surface of the plugs in the tubes was placed the junction of a Pt-Rh thermocouple in a porcelain tube, the end of which had been ground down to a thickness of 0.4 mm. to avoid lag from the porcelain wall. Movable plugs of graphite $\frac{3}{16}$ inch thick were mounted on tiny carbon rods which were marked to show the distance of the nearer surface of that plug from that of the stationary plug. By setting these 3 inches out we can determine by the optical pyrometer (the Wanner was used) the temperature in each tube corresponding to the temperature of the charge itself 3 inches from the core, as shown by the thermocouple. The couple had been carefully calibrated. By setting the movable plugs at varying distances, the gradient through each tube could be determined.

The record of the run follows:

Time.	K. W.	Temp. stationary plugs.			Temp. movable plugs 3" out.			Temperature charge 3" out by couple. Degrees.
		Carbon. Degrees.	Graphite. Degrees.	SiC. Degrees.	Carbon. Degrees.	Graphite. Degrees.	SiC. Degrees.	
7.37	20
7.52	3.5	1050	985	1060	50
7.56	..	1100	1040 ¹	1140	90
8.00	6.7	1310	1240	1330	100 ²
8.18	15.6	1030	1055	below 900	485 ²
8.22	15.6	1040	1135	1014	780 ²
8.25	12.9	1785	1785	1785	1110	1175	1055	950 ²
8.30	10.3	1770	1770	1770	1160	1190	1110	1110
8.36	..	1755	1740	1755	1175	1245	1160	1170
8.45	23.0
8.50	14.0	2005	2005	2005	1415	1440	1370	1380
8.55	1430	1455	1380	1390
9.00	16.1	1960	1930	1945	1455	1470 ³	1415	1420
9.05	15.8	1470	1490	1440	1450
9.15	1525	1550	1480	1485
9.20	16.0	1550	1570	1505	1495
9.30	15.4	.. ⁴ ⁵

¹ The projecting end of the graphite tube hisses when water is dropped on it. The others do not at this time.

² Thermocouple lag affects these readings. They were increasing at a much more rapid rate than those of the Wanner on the movable plugs.

³ Graphite tube red hot outside furnace, others not. One could bear the hand on top of furnace charge at this time.

⁴ Carbon tube disintegrating to powder and fuming. No more readings made on it.

⁵ Thermocouple taken out at this point. Readings continued on graphite and SiC tubes.

TABLE II.

Time.	K.W.	Temp. in graphite tube.				Temp. in SiC tube.							
		At stat. plug.	1" back.	2" back.	3" back.	At stat. plug.	$\frac{1}{2}$ " back.	1" back.	$1\frac{1}{2}$ " back.	2" back.	$2\frac{1}{2}$ " back.	3" back.	
9.35	..	2000	1885	1730	1580	2000	..	1860	..	1670	..	1515	
10.70	22.3	2220	2100	2005	1930	1830	1755	1600	

Table III shows the deviations of the temperatures of the three tubes at the 3-inch point from that of the furnace itself after thermocouple lag had been overcome.

The carbon tube was much disintegrated at the end of the run, the graphite a little less so, while the SiC tube was in good shape. The glass tube attached to

the graphite tube had almost fused shut, while those in the others had not softened.

It will be seen that the heat conductivity of the graphite tube is too great, both by the rapidity with which the stationary plug reading in that tube would fall when the power input was reduced by altering the field rheostat of the generator, and by the fact that the projecting end of the tube was red hot when the furnace itself at that point was comparatively cold, as well as by the figures given.

The graphite gives too flat a gradient, that through the furnace being much steeper. The heat flow through the graphite was so great that at a rapid rate of heating, as at the first of the run, the readings on the graphite tube stationary plug were much too low. The movable plug readings were all too high, for the same reason.

The carbon tube was better, but still introduces serious error. The SiC tube gave uniformly good results, the agreement with the thermocouple in the charge itself holding for the range of 400° investigated and for a fifty-minute run.

In the work of Tucker and Lampen,¹ a graphite tube was placed transversely through a small carborundum furnace, the temperature gradient determined by sighting on a movable plug with a Wanner, and when the run was over, cutting down through

the furnace and measuring the width of the graphite, carborundum and siloxicon zones.

The thickness of the zone was then compared with the graph of the gradient, and the following figures obtained. Decomposition of SiC to graphite 2218° and 2223°, formation of SiC, 1980° and 1920°.

¹ Loc. cit.

TABLE III.

Deviations in degrees C.

Temp. by couple.	Carbon.	Graphite.	SiC.
1110	0	+80	0
1170	+5	+75	-10
1380	+35	+60	-10
1390	+40	+65	-10
1420	+35	+50	-10
1450	+20	+40	-10
1485	+40	+65	-5
1495	+55	+75	+10
average deviation	+30	+65	-5

Changing Tucker's readings into inches from the edge of the core instead of centimeters from the center, so as to make them comparable with the figures given in Table III, we get:

TABLE IV.—TUCKER'S GRAPHITE TUBE.

Distances from core	0"	1/2"	1"	1 1/2"	2"	2 1/2"	3"
Temp. degrees.....	2240	2130	2060	1980	1900	1810	1750

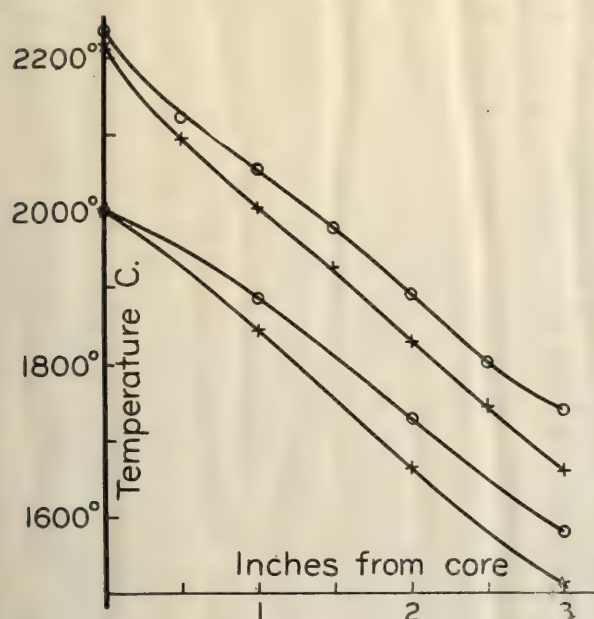


Fig. 2.—Temperature gradients: circles denote graphite tubes; crosses, carborundum tubes.

The data of Tables III and IV are plotted in Fig. II. The circles denote temperatures read in the graphite tubes and the crosses those in SiC tubes. In the run plotted by Tucker, from which the figures in Table IV are taken, he found SiC on one side of the furnace at 1940° and 1900° on the other. He averages this and calls it 1920°. Another run gave him an average of 1980°, the individual readings on which this was based not being given. He then averages the averages and gets 1950°.

Owing to the disregard of the difference in the furnace and tube gradients in Tucker's work, it is plain that even his lowest figure for the formation temperature of SiC must be too high. His furnace took only 18 lbs. of charge against 150 in ours, and his graphite tube was smaller. In the run for which data was given, the temperature at the edge of his core was 20° higher than in the run given in our Table VI, but the conditions are still roughly comparable. From Fig. II it is seen that 1900°, his lowest figure for

SiC, would correspond to a temperature in the SiC tube, or in the furnace, of about 1830°. Since his tube was graphite it would be expected that his figure for the graphite point, 2220°, would be correct, since the gradient there would not vary much from that in the furnace.

A series of experiments having shown us at about what temperatures graphite, SiC and siloxicon were formed in the SiC furnace, runs were made with two temperature tubes in the furnace, one plug being 1/4 inch further from the core than the other. The runs lasted 2 1/4 hours, the temperature being carefully controlled by regulating the power input, so that the last 50° rise took twenty minutes and the last 20° took ten minutes. The object was to get the line of demarcation between the zones to be just between the two temperature plugs. Knowing the temperatures to which the two plugs had been raised, we could get within fairly narrow limits the temperature of formation of each product.

Three runs were thus made, A, B and C. In A for the formation temperature of SiC, the plugs were placed with their backs 3/4 inch and 1 inch from the core; in B, for graphite 1/4 inch and 1/2 inch; and in C, for siloxicon, 2 3/4 inch and 3 inch. When the tube showed that the maximum temperatures desired had been reached, the run was stopped and, after cooling, the furnace examined.

Table V gives the temperatures read on the inner surface of the plugs—and incidentally shows the agreement of the three pyrometers which had been separately calibrated.

TABLE V.
Tube nearer core.

Run.	By Wanner. Degrees.	By Morse. Degrees.	By Thwing. Degrees.	Aver. Degrees.
A.....	1820	1823	1825	1822
B.....	2240	2230	2230	2233
C.....	1547	1550	..	1548

Tube farther from core.

Run.	By Wanner. Degrees.	By Morse. Degrees.	By Thwing. Degrees.	Aver. Degrees.
A.....	1790	1800	1800	1797
B.....	2190	2180	2180	2183
C.....	1526	1520	..	1523

The correction for drop in temperature through the 3/16" plug at this rate of heating, is +25° at 1800°, +17° at 2200° and +31° at 1550°. This gives us the corrected values.

TABLE VI.

Run.	Nearer tube. Degrees.	Farther tube. Degrees.
A.....	1847	1822
B.....	2240	2210
C.....	1579	1554

In run A, crystalline SiC was well past the end of the nearer tube, and just to the farther one, a solid wall of SiC remaining just back of that plug when the tube was taken out. In B, the nearer tube had graphite on it, 1/8 inch past the end, while the farther one was 1/8 inch outside the graphite zone. In C, siloxicon was found 1/4 inch past the end of the nearer tube and 1/8 inch past the former, so even the latter

temperature is a trifle above the formation point of siloxicon.

From this we deduce the following figures:

Decomposition point of SiC to graphite $2220^{\circ} \pm 20^{\circ}$;

Formation of crystalline SiC $1820^{\circ} \pm 20^{\circ}$;

Formation of siloxicon $1540^{\circ} \pm 30^{\circ}$.

The value for siloxicon is not established within as close limits as the others because of greater difficulty in telling where the zone really begins. All these values were checked by repeated runs.

Tucher's figure for graphite agrees exactly with ours, and his lower figure for SiC, when corrected for the error due to the use of a graphite tube, comes within 10° of our value. One figure, 1980° , obtained by him for this point is 160° out because of the difference in the gradients in tube and furnace. This shows how large an error disregard of this point may introduce into temperature measurements in electric furnace work.

We have not attempted to fix any formation temperature for the so-called "Amorphous Carborundum" that is said to occur between the zones of crystalline SiC and of siloxicon, as there is no way of telling where the "amorphous SiC" zone begins or ends. Belief in the existence of this seems to have been handed down through the literature from the first work of Mulhauser.¹

He analyzed a sample taken just outside the crystalline SiC zone, and after long treatment with HF and ignition, found it to correspond fairly well with the formula SiC. Potter² has shown that siloxicon is attacked by HF and ignition with elimination of Si and O, leaving a residue that approximates the formula SiC. It seems very doubtful if amorphous SiC is formed in the commercial furnace, the zone outside the crystallized SiC probably being a series of complex oxycarbide compounds or solid solutions grouped under the name of siloxicon.

This work was done at Cornell University in the Spring of 1910 under the direction of Prof. Bancroft, to whom the writer's best thanks are due.

DETROIT, MICH.,
Feb., 1911.

ANALYSES OF CHARACTERISTIC NORTHWEST TIMBER SOILS.

By J. S. JONES.

Received January 23, 1911.

In the northwestern states large areas of cut and burned-over timber lands are being rapidly cleared and brought into a state of cultivation. For the most part these lands have produced splendid growths of white and yellow pine, fir, tamarack, and cedar. They will, in time, become of great importance to the agricultural development of the Northwest. In many localities they have already reached a stage in their development which indicates, that, as a class, the timbered soils of the Northwest will present problems peculiar to themselves. As a first step to a better understanding of these lands, we have

recently made complete analyses of samples representing several distinct soil types, embraced in the timber belt of north Idaho, locally referred to as the Pan Handle. Since up to this time no data have been published relative to the composition of any of these timber lands, we submit the following analyses in the belief that they will be of interest to others engaged in soil investigations.

If comparisons are suggested by these analyses, it should be noted that the lands in question lie entirely in the humid section of the state. The fine soil only (that which passed the meshes of a $\frac{1}{2}$ mm. sieve) was used for analysis. The samples were digested for ten hours in a boiling water bath with hydrochloric acid of 1.115 sp. gr., 10 cc. of acid being used for each gram of soil. The analysis of the hydrochloric acid solutions, in the main, was conducted in accordance with the methods outlined by the Association of Official Agricultural Chemists. The humus determinations were made on solutions filtered through Pasteur-Chamberland filter tubes.

TABLE I.—PERCENTAGE COMPOSITION OF TIMBER SOILS.¹

Laboratory number.	Bench Land.						
	360a	360b	360c	360d	360e	360f	204
Coarse soil...	30.00
Fine soil...	100.00	100.00	100.00	100.00	100.00	100.00	70.00
CHEMICAL ANALYSIS OF FINE SOIL.							
Insoluble matter...	84.690	84.030	82.550	82.230	78.830	84.520	82.79
Potash (K ₂ O)	0.318	0.283	0.302	0.310	0.360	0.321	0.30
Soda (Na ₂ O)	0.229	0.226	0.276	0.282	0.292	0.276	0.24
Lime (CaO)	0.407	0.436	0.590	0.407	0.918	0.415	0.81
Magnesia (MgO)...	0.623	0.516	0.623	0.734	0.846	0.878	0.42
Iron Oxide (Fe ₂ O ₃)...	3.490	3.300	3.530	3.350	3.820	3.520	2.26
Alumina (Al ₂ O ₃).....	6.039	6.275	6.618	6.655	6.943	6.139	7.46
Phosphoric acid (P ₂ O ₅)	0.285	0.305	0.302	0.425	0.237	0.271	0.43
Sulphur trioxide (SO ₃)	trace	trace	trace	trace	trace	trace	0.04
Carbon dioxide (CO ₂)
Volatile matter.....	4.300	4.676	4.930	5.580	7.770	3.957	5.70
Total....	100.381	100.047	99.721	99.973	100.016	100.297	100.45
Reaction.	slightly acid.	slightly acid.	slightly acid.	slightly acid.	slightly acid.	slightly acid.	slightly acid.
Total nitrogen	0.044	0.054	0.050	0.080	0.170	0.042	0.10
Humus.....	0.702	0.773	0.740	1.730	1.620	0.542	1.36
Humus nitrogen p.c. in humus....	4.830	4.430	4.330	3.300	6.640	5.250	6.62
Humus nitrogen p.c. in soil..	0.034	0.034	0.032	0.057	0.107	0.028	0.08

The samples whose analyses appear in Table I, represent to a depth of 15 inches the soils of typical bench lands in the northernmost county of the state. Samples No. 360a-360f, inclusive, were taken at various places along the "divide" which separates the valleys of the Pend d'Oreille and Kootenai Rivers, and which here has an elevation of approximately 2000 feet. The crest of the "divide" is perhaps 150 feet higher than the broad valleys on either side. More precisely the area represented by these samples lies from twenty

¹ Z. angew. Chem., 1893, 641; J. Am. Chem. Soc., 15, 411 (1893).

² Trans. Am. Electrochem. Soc., 12, 191 (1907).

¹ For the analyses which are recorded in Table I, credit is due Mr. H. P. Fishburn.

to twenty-five miles northeast of the town of Sandpoint. A large portion of it will be utilized in the immediate future for orchard purposes. Physically, the surface soil may be described as a fine sandy loam. This at a depth of 20-24 inches shades into a light clay loam. A vertical excavation to a depth of 10-12 feet failed to reveal any material change in the physical characteristics of the under soil. A large portion of the area has been fire-swept, the blackened stumps and prostrate trunks of trees still bearing testimony to the splendid growth of yellow pine and cedar which it has produced.

Sample No. 204 represents similar bench land on the west side of Pend d'Orielle Lake, and approximately ten miles southeast of the town of Sandpoint. This bench has an elevation of 150-200 feet greater than the level of the lake. From it the heavy timber has been logged and a dense growth of underbrush has taken its place. This section has not recently been burned over.

TABLE II.—PERCENTAGE COMPOSITION OF TIMBER SOILS, VALLEY LANDS.

Laboratory number.	145a	145b	145c	145d	145e
Coarse soil.....	35.00	8.00	30.00
Fine soil.....	100.00	100.00	65.00	92.00	70.00

CHEMICAL ANALYSIS OF FINE SOIL.

Insoluble matter.....	74.36	43.40	70.05	67.26	64.09
Soluble silica.....	12.15	26.28	11.96	12.14	15.60
Potash (K_2O).....	0.66	0.44	0.25	0.35	0.39
Soda (Na_2O).....	0.45	0.34	0.57	0.39	0.53
Lime (CaO).....	0.90	0.10	0.63	0.61	0.58
Magnesia (MgO).....	trace	trace	trace	trace	0.74
Iron oxide (Fe_2O_3).....	3.04	4.44	3.27	3.70	4.35
Alumina (Al_2O_3).....	5.86	10.13	6.45	7.53	5.32
Phosphoric acid (P_2O_5).....	0.09	0.15	0.56	0.28	0.28
Sulphur trioxide (SO_3).....	none	none	none	none	none
Carbon dioxide (CO_2).....
Volatile matter.....	3.09	14.37	6.09	6.23	7.81
Total.....	100.60	99.65	99.83	98.49	99.69
Total nitrogen	none	0.16	0.08	0.11	0.17

Samples No. 145a-145e, inclusive, represent the bottom lands on the south side of the Pend d'Orielle River not far from the Idaho-Washington State line. This area has been cleared of a heavy growth of yellow pine, cedar, and underbrush. Like the bench land previously mentioned it is being developed for orchard purposes.

No. 145a represents a very light colored soil. Near the river it appears as a surface soil, but for the most part it is the characteristic subsoil of that section. This sample was taken to a depth of 15 inches. No. 145c represents a soil of similar character farther back from the river. This one apparently results from the first coming very close to the surface, and having incorporated with it more or less of the alluvium carried down from the adjacent hillsides. Nos. 145b, 145d, and 145e are representative of alluvial and colluvial soils carried into the valley from the near-by hills, and deposited evenly to a considerable depth upon No. 145a. These samples were likewise taken to a depth of 15 inches.

Still another type of timber land is represented in our analyses. This characterizes extensive areas of the higher lands embraced in and bordering the Coeur d'Alene Indian Reservation on the south and south-

east. This district is covered with a heavy growth of yellow pine and fir. It is very rolling in character, but has an average elevation of 2500-3000 feet. The soil, in depth and physical properties, resembles very closely the prevailing types of the adjacent open prairie country, also a very rolling one, known locally as the "Palouse."

TABLE III PERCENTAGE COMPOSITION OF TIMBER SOILS, HIGH LAND

Laboratory number.	200	201a	201b.
Coarse soil.....
Fine soil.....

CHEMICAL ANALYSIS OF FINE SOIL.

Insoluble matter.....	71.38	70.00	72.77
Soluble silica.....	7.89	9.85	8.34
Potash (K_2O).....	0.63	0.57	0.60
Soda (Na_2O).....	0.50	0.50	0.41
Lime (CaO).....	0.73	0.83	0.86
Magnesia (MgO).....	1.00	0.82	0.78
Iron oxide (Fe_2O_3).....	8.09	8.27	9.65
Alumina (Al_2O_3).....	4.24	4.00	2.64
Phosphoric acid (P_2O_5).....	0.32	0.24	0.25
Sulphur trioxide (SO_3).....	trace	trace
Carbon dioxide (CO_2).....
Volatile matter.....	5.70	5.31	4.00
Total.....	100.48	100.39	100.30
Total nitrogen.....	0.06	0.07
Humus.....	1.08	0.92

No. 200 represents a district of somewhat greater elevation than that represented by either of the others.

No. 201a represents the yellow pine lands more particularly, and was taken to a depth of 24 inches on a southwesterly slope. No. 201b was taken to an even greater depth on a north hill slope, and is typical of the fir lands. Both Nos. 201a and 201b represent cut-over timber lands, but neither one has ever been in cultivation. Soil in adjacent fields and identical in character with that represented by 201a has been in cultivation for several years and grows darker in color with cultivation. Cultivated soil similar to that represented by No. 201b has not changed perceptibly in color during the several years it has been under cultivation. It has also been noticed that soils represented by No. 201a compact readily, and that those represented by No. 201b persistently remain loose and open. On the crest of the hills these soil types blend. When cleared of stumps and underbrush this land will be converted into grain and timothy farms.

With soil investigators, an opinion seems to be prevalent that pine forest soils, as a class, are weak in the essential elements of plant nutrition. The analyses recorded above, however, indicate very clearly that extensive areas of typical pine forest soils of the Northwest are well supplied with all of the mineral elements required in plant growth, and are exceptionally rich in phosphoric acid. As a rule, they are slightly acid in reaction, and, although substantial amounts of calcium are present, the application of finely crushed limestone is known to be of decided advantage in bringing them into a good state of cultivation.

INVESTIGATIONS ON THE ESTIMATION OF INORGANIC PHOSPHORUS IN ANIMAL TISSUES.

By A. C. WHITTIER.

Various methods and modifications for the extraction and the determination of inorganic and organic forms of phosphorus in animal tissues have been published, but there seems yet to be a lack of agreement in the work of the different investigators. A sharp separation of organic from inorganic phosphorus in the tissues, in the proportions present at the time of death, is rendered very difficult, owing to the chemical changes taking place in the tissues themselves as well as changes induced by agents employed in the estimation of these compounds.

In 1905 Emmet and Grindley¹ published a method for the determination of inorganic phosphorus in cold water extracts of flesh. The essentials of their method were (1) the condensation of a measured portion by heat, (2) the removal of the resulting coagula by filtration, (3) the precipitation of the inorganic phosphates with neutral ammonium molybdate after adding a minimum amount of nitric acid, (4) the reprecipitation of the dissolved precipitate by acid ammonium molybdate. The determination was completed in the regular gravimetric way for phosphorus.

Almost simultaneously Siegfried and Singewald² published work done on flesh extracts. They recommended a method for the separation of inorganic and organic phosphorus consisting of a preliminary precipitation of the inorganic phosphates with barium chloride and ammonia; after precipitation was complete, the barium phosphate was filtered out. Organic phosphorus was determined on an aliquot of the filtrate and inorganic phosphorus obtained by difference.

Early in 1910 Forbes, *et al.*,³ published a method for the extraction and determination of inorganic phosphorus applicable to muscle, liver, kidney and brain.

The extraction was accomplished by boiling the sample in ammonium sulphate solution, followed by repeated extractions with hot water. The determination was made by precipitating the inorganic phosphates with magnesia mixture and ammonia followed by the regular gravimetric method for phosphorus on the dissolved magnesium precipitate.

This method gave almost identical results with and without the application of heat to cold water extracts of flesh and agreed with results obtained by the Emmet and Grindley method.

Using the Siegfried and Singewald method, Stanley and Trowbridge's⁴ results showed that any method involving the use of heat previous to the separation of the organic and inorganic forms of phosphorus would give too high a figure for inorganic phosphorus in flesh extracts.

Working on beef loaf, these authors found only a trace of organic phosphorus after coagulating the extract by boiling.

Emmet and Grindley made determinations on cooked and uncooked samples of flesh, but their results show no such wide variations for organic phosphorus as do the results of Stanley and Trowbridge which they obtained with and without the application of heat.

With such a diversity of results by different workers it seems desirable to collect additional data on this question. Our first work in this study was to compare the method used by Stanley and Trowbridge with the magnesia method used in this laboratory, employing magnesia mixture as a preliminary precipitating reagent.

An attempt to estimate the inorganic phosphorus directly on the washed barium phosphate precipitate was abandoned because of the white precipitate washing through the filter paper, more especially in the case of extracts of raw meat. This made it necessary to make the determination of the soluble organic phosphorus on an aliquot of the unwashed filtrate from the barium precipitation of inorganic phosphates. In order to obtain the inorganic phosphorus figure, it is then necessary to make determinations of the total soluble phosphorus and by difference calculate the inorganic phosphorus content.

TABLE I.—COMPARISON OF THE BARIUM AND MAGNESIUM METHODS ON COAGULATED AND UNCOAGULATED FLESH EXTRACTS.

Description of sample.	Total phosphorus.	Phosphorus soluble in cold water.	Inorganic phosphorus.					
			Magnesium.			Barium		
			Before coagulation.	After coagulation.	Hot water extract.	Per cent. of total soluble before coagulation.	Per cent. of total soluble after coagulation.	
Pork steak (a)	0.223	0.173	0.131	0.136	...	76.9	76.9	0.115 ¹
			0.133	0.132	...	76.9	76.9	0.118 ¹
			0.136	0.130	...			0.094 ¹
Beef round (b)	0.220	0.162	0.113	0.122	...	70.4	72.2	0.111
			0.113	0.117	...	70.4	72.2	0.102 ¹
			0.115	0.117	...			0.120
Beef round (c)	...	0.173	0.098	0.106	0.108	57.8	60.1	0.102 ¹
			0.100	0.103	0.111	57.8	60.1	0.109
			0.100	0.104	0.110			0.106
								0.114
								0.106
								0.107

Fairly concordant results were obtained by the barium method, provided that the extract was first coagulated by boiling, or that the filtrate from the uncoagulated extract could be obtained perfectly clear on filtering off the barium phosphate precipitate.

This is in accord with the findings of Siegfried and Singewald who say, "Von den Filtraten, welch absolut klar sein müssen....."

Stanley and Trowbridge say: "The samples from the raw meats gave very little precipitate and the filtrates were in every case slightly cloudy."

Doubled No. 589 blue ribbon filter papers were used, but with uncoagulated extracts the filtrates from the barium phosphate precipitation were cloudy. In two instances, however, as noted in the preceding table, clear filtrates were obtained by repeated filtering and the results on these clear filtrates give very nearly identical figures with those obtained by the same method on boiled extracts of the same sample. These

¹ Filtrates from barium precipitation cloudy.

¹ J. Am. Chem. Soc., 28, 25.

² Z. Nahr. Genussm., 9, 521.

³ Bull. 215, 481, Ohio Agr. Exp. Sta.

⁴ THIS JOURNAL, 2, 212.

two results are also in close agreement with determinations on both boiled and unboiled extracts of the same sample by the magnesium method.

Briefly stated, the objections to the barium method for inorganic or organic phosphorus determinations on flesh extracts, especially cold water extracts of raw meats, are:

(1) The probable retarding action of the proteids contained in a cold water extract on the precipitation of the inorganic phosphates by barium chloride and ammonia.

(2) The possibility that the organic material precipitated along with the barium phosphate contains organic phosphorus.

(3) The difficulty encountered in filtering off the barium phosphate precipitate. A cloudy filtrate from the barium phosphate precipitation gives a high figure for organic phosphorus.

(4) Its mechanical imperfections and length make it objectionable for a routine method.

After using barium chloride and ammonia in comparison with magnesia mixture as a preliminary precipitant of inorganic phosphorus, the writer concluded that magnesia was by far the better reagent to use in the further comparison of heated and unheated extracts of tissues, the chief reasons being:

(1) Less organic matter was thrown down with magnesium than with barium.

(2) The precipitate settled quickly.

(3) Filtration was rapid and gave a clear filtrate.

(4) The direct determination of inorganic phosphorus on the washed precipitate, with magnesia mixture as a precipitant, is much briefer than the indirect method by the use of barium chloride and ammonia.

Great difficulty was experienced in getting enough clear cold water extracts of liver, kidney and brain to make comparisons of coagulated and uncoagulated extracts. This was finally accomplished on samples D, E, F, and G by the use of a Berkefeld filter.

Approximately 80 grams of finely ground sample was weighed out into a large beaker. A small amount of distilled water was added and the contents beaten up thoroughly with a stirring rod. The sample was then transferred to a graduated liter flask by the use of about 500 cc. of distilled water. This was shaken for about 30 minutes and then filled to the mark, poured into a large flask and made up to four liters. After shaking every five minutes for one hour the contents were allowed to settle and the supernatant liquid was poured into a Berkefeld filter. This gave a clear extract, but in the case of the brain it came through very slowly.

These samples were purchased from the local butchers and were at least two or three days' old.

In order to learn whether or not organic phosphorus changes to the inorganic state to any appreciable extent before determinations could be made on a routine scale after the death of an animal, a young pig was killed and the estimations on the different tissues were started immediately. Samples of the blood were caught in weighed bottles, the entire

contents of each bottle being used for a determination. This insured a representative sample. The other tissues were immediately removed from the carcass, ground, sampled and weighed out in the least possible time.

Cold extracts were made only on the muscle (H) of the ham, while the regular method as outlined in our previous article¹ was employed on all the tissues named, including the sample of muscle for the sake of further comparison. The sample of muscle (H) was kept on ice for 24 hours and the determination repeated in the same way as on the first day.

TABLE II.—COMPARISON OF COAGULATED AND UNCOAGULATED EXTRACTS OF ANIMAL TISSUES. USING THE MAGNESIUM METHOD.

Description of sample.	Inorganic phosphorus.								
	Total phosphorus.	Water-soluble phosphorus.	Per cent. of total which is soluble in cold water.	Before coagulating.	After coagulating.	Boiling (NH ₄) ₂ SO ₄ extract.	Per cent. of soluble before coagulating, which is inorganic.	Per cent. of soluble after coagulating, which is inorganic.	Per cent. of total after coagulating, which is inorganic.
Pig muscle									
H 1st day...	0.227	0.166	73.1	0.110	0.121	0.120	65.1	74.1	54.2
Pig muscle									
H 2nd day...	0.227	0.168	74.0	0.130	0.137	0.130	77.4	81.5	60.4
Beef kidney D...	0.237	0.093	39.2	0.076	0.075	...	81.7	80.6	31.7
Beef kidney E...	0.238	0.102	42.9	0.071	0.076	...	69.6	74.5	31.9
Beef liver F...	0.367	0.136	37.1	0.098	0.099	...	72.1	72.8	27.0
Calf brain G...	0.296	0.078	26.4	0.055	0.053	0.060	70.5	68.0	17.9
Pig brain J...	0.370	0.060	16.2
Pig liver K...	0.324	0.070	21.6
Pig blood L...	0.054	0.0186	34.4

In the majority of cases the preceding table shows that where heat is applied a slight increase in per cent. of inorganic phosphorus occurs. The differences are small where they exist at all and in the writer's opinion are due, not to a change of organic to inorganic phosphorus, but to a better precipitation of the inorganic phosphates from the clearer solutions produced by coagulation.

The cold water extract of sample (H) (first day) gave a considerably lower figure for inorganic phosphorus than did the same extract on coagulation. This was possibly due to the larger amount of organic matter in this extract than is usually present, as this extract was prepared from the sample before rigor mortis had set in and was slightly milky in appearance. It is believed this condition prevented complete precipitation with magnesium mixture. It should be noticed, however, that the coagulated cold-water extract gave identical results with the hot ammonium-sulphate-extract.

If there is a progressive splitting up of the organic compounds of phosphorus by heat, one would expect a much higher figure for inorganic phosphorus from an extract procured by boiling the whole sample than from a cold-water extract which is simply coagulated by boiling. This is not the case, however, since hot-water extracts gave the same figure as did the coagu-

¹ Bull. 215, 487, Ohio Agr. Exp. Sta.

lated cold-water extracts. Sample H, on the second day, gave somewhat higher results for inorganic phosphorus than on the first day immediately after the death of the animal. This was probably due to enzyme or bacterial action, or to both.

The cold-water extract from sample b, Table I, contained 0.119 per cent. inorganic phosphorus after coagulation. This extract after boiling for 2 hours with 0.2 per cent. HCl gave 0.121 per cent. of inorganic phosphorus, but determinations made after the extract had stood 36 hours in the laboratory gave a result of 0.141 per cent. inorganic phosphorus. Either enzymes or bacteria, or both, increased the inorganic phosphorus one-sixth of the original amount, while boiling with acid made no appreciable difference.

This is in accord with results obtained by Siegfried and Singewald.

CONCLUSIONS.

Stanley and Trowbridge's determinations of organic phosphorus by the barium method are too high on uncoagulated extracts on account of barium phosphate passing through the filter.

The temperature of boiling water has very little hydrolyzing action on the organic compounds of phosphorus in animal tissues.

Enzymes and bacteria seem to exert more of a hydrolyzing influence on organic phosphorus compounds of animal tissues than does boiling.

Coagulation of the proteids by boiling the extracts of tissues serves two purposes: (1) it clears the solution—a more complete precipitation resulting; (2) it arrests the action of enzymes and bacteria.

ACKNOWLEDGMENTS.

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A VOLUMETRIC METHOD FOR ANTIMONY IN ALLOYS.

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The object of this paper is to describe an application of L. W. Andrews' iodate method¹ to the determination of antimony in alloys, particularly "hard leads" and solders. The method is satisfactory because it is not interfered with by copper and iron, metals which frequently occur in small quantities in these alloys, and because it is rapid and accurate.

Two other iodimetric methods have been compared with this by the writer with less satisfactory results. The first, which is based upon getting the antimony into the pentavalent form in dilute hydrochloric acid solution, adding potassium iodide and titrating with sodium thiosulphate, gave good results in the absence of copper and iron, but was unsatisfactory in the presence of these metals. The other method, depending upon getting the antimony into the trivalent state in a sodium bicarbonate solution and

titrating with iodine was found to give poor results, particularly with alloys containing much lead, as even when tartaric acid is used, the lead carbonate precipitate appears to hold antimony, thus causing low results.

Andrews showed¹ that his iodate method was satisfactory for antimony by applying it to pure tartar emetic. The method has been further tested by the writer by dissolving weighed quantities of Kahlbaum's pure antimony in concentrated sulphuric acid and titrating it as described beyond. It is to be observed that this titration is carried out in the presence of 15–20 per cent. of actual hydrochloric acid, which gives iodine monochloride as the end-product, according to the equation $2\text{SbCl}_3 + \text{KIO}_3 + 6\text{HCl} = 2\text{SbCl}_5 + \text{KCl} + \text{ICl} + 3\text{H}_2\text{O}$. The potassium iodate solution which was used throughout the entire investigation contained 3.5667 grams of KIO_3 per liter, corresponding to 0.00400 gram of antimony for 1 cc.

The following results were obtained:

Sb taken. Gram.	KIO_3 used.	Sb found.
0.1000	24.85	0.0994
0.1000	24.90	0.0996
0.0490	12.20	0.0488

The following method of analysis for alloys has been worked out: Take 0.5 gram of alloy in the form of drillings or chips² in a 200 cc. Erlenmeyer flask. Add 10 cc. of concentrated sulphuric acid and heat until the alloy is entirely decomposed.³ Boil the solution gently for about 2 minutes after the lead sulphate has become white, allow the solution to cool to room temperature, dilute with 15 cc. of cold water, allow to cool somewhat, add 15 cc. of 1 : 1 hydrochloric acid, shake thoroughly and filter off the lead sulphate on a Gooch crucible, washing with small quantities of the same hydrochloric acid. Transfer the filtrate to a glass stoppered bottle of about 250 cc. capacity, add 5 cc. chloroform, 15 cc. of concentrated hydrochloric acid,⁴ and 5 cc. of iodine monochloride solution.⁵ Shake the titration bottle, let it stand for about five minutes and then titrate the liberated iodine with standard potassium iodate solution⁶ until the chloroform is just decolorized after thorough shaking, which should be repeated in about a minute to make sure of getting the true end point. To make a second titration most of the liquid may be poured off, leaving the chloroform ready for use.

It should be observed that, as Andrews¹ has shown,

¹ *Loc. cit.*

² If the alloy contains less than 2 per cent. of antimony, it is better to take 1 gram or more, while with alloys very rich in antimony 0.1 or 0.2 gram will suffice.

³ If the flask is covered with an inverted porcelain crucible cover, the dissolving and boiling may be carried out without the escape of any disagreeable quantities of fumes, so that the hood need not be used.

⁴ To allow for dilution with the standard solution.

⁵ To prepare this solution, dissolve 10 grams of potassium iodide and 6.44 grams of potassium iodate in 75 cc. of water, add 75 cc. of concentrated hydrochloric acid, then add a globule of chloroform in a glass stoppered bottle, and adjust exactly to a faint iodine color by shaking and adding dilute potassium iodide or potassium iodate solution as the case may require.

⁶ If the volume of potassium iodate solution used is much over 15 cc., it is advisable to add more concentrated hydrochloric acid to keep the strength near the 1 : 1 point.

the strength of the hydrochloric acid solution in which the titration is made is of much importance. The directions, therefore, as given above should be closely followed in regard to the strength and amounts of hydrochloric acid used.

The following results were obtained with a number of alloys:

No.	Weight taken.	cc. KIO ₃ used.	Per cent. of Sb.	Per cent. of Sb by thiosulphate method.
1A	0.2000	6.70	13.40	13.43
2A	0.2000	6.70	13.40	...
1B	0.2000	6.00	12.00	12.07
2B	0.2005	6.03	12.03	...
1C	1.0000	2.70	1.08	1.04
2C	1.0000	2.70	1.08	...
1D	0.5000	5.90	4.72	5.11 ¹
2D	0.5000	5.90	4.72	...
1E	1.0000	2.40	0.96	0.96
1F	0.5000	2.85	2.28	2.32
2F	0.5000	2.85	2.28	...
1G	1.0000	2.80	1.12	1.16

The first two alloys are antimonial leads and the others are commercial solders, some of which were of poor quality on account of the antimony present.

The time required for an analysis was about an hour.

Arsenic is rarely present in appreciable quantities in the alloys under consideration, but it is to be noticed that, if present, it would be titrated with the antimony. The following results were obtained by dissolving metallic arsenic in concentrated sulphuric acid and proceeding exactly according to the method that has been given.

As taken.	KIO ₃ used.	As found.
Gram.	cc.	
0.0100	4.10	0.0102
0.0100	4.10	0.0102
0.1019	40.60	0.1015

In a case where an alloy contains an appreciable amount of arsenic it is best to carry out the process exactly as directed as far as filtering off the lead sulphate and washing it with 1:1 hydrochloric acid. Then pass in hydrogen sulphide to precipitate the arsenic, pass air through the liquid for half an hour or so to remove the hydrogen sulphide and to oxidize any iron that may be present, filter, wash with 1:1 hydrochloric acid, and titrate as usual. This process was tested by the use of alloys mixed with known quantities of pure metallic arsenic with the following results:

Alloy taken.	As taken.	Per cent.	Per cent.
Gram.	Gram.	Sb found.	Sb in alloy.
0.5000	0.0050	4.72	4.72
0.9560	0.0118	4.77	4.72
0.2000	0.0460	12.00	12.00
0.2000	0.0520	12.10	12.00
1.0000	0.0097	1.04	1.08

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DETERMINATION OF COCOA SHELLS IN COCOA POWDER.

By W. L. DUBOIS AND C. I. LOTT.

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The work herein described was undertaken to test a method proposed by Goske.² This procedure

¹ Solder D contained a little copper or iron which caused the thio-sulphate method to give high results. Also alloys A and B were found to contain traces of copper.

² *Z. Nahr. Genussm.*, 19, 154; *C. A.*, 4, 1328 (1910).

depends upon the fact that the heavier constituents of cocoa shells sink in a solution of calcium chloride of specific gravity 1.535, whereas the lighter constituents of the cocoa float in the same. The parts sinking are dried and weighed. Goske determined the amount of heavy material in a number of varieties of cocoa shells of known purity and found this value to vary from 15.4 to 38.76 per cent. on the fat-free shell. The highest figure is taken as the basis of calculation when applying the method to cocoa. The weight of the heavy shell constituents, calculated to fat-free cocoa, is divided by the factor 38.7 and multiplied by 100, to give the percentage of shells in the cocoa.

In studying this method, the writers determined factors on a number of varieties of cocoa shells, after extracting the fat. In the table below is given the results obtained:

No.	Variety of cocoa shells.	Percentage heavy constituents, sp. gr. over 1.535.
1	Maracaibo	22.72
2	Guayaquil	21.26
4	Caracas	32.32
5	Bahia	39.68
6	African	31.44
7	Sancher	36.66
8	Surinan	43.52
9	Java	42.7
10	Arriba	39.46
11	Venezuela	33.62
12	Trinidad	52.2
13	Pto Cabello	48.12

The average of the figures above is 36.96. The factor selected, therefore, for the determination on cocoa powders was 37.

It will be noted that shell No. 2 showed the lowest percentage of heavy constituents, No. 12 the highest, and that No. 7 was the nearest to the average. These three shells were added in known quantities to a cocoa powder on which the fat and shell content—the latter by Goske's method—were first determined. With these mixtures Goske's method was followed identically as laid down, with the results shown in the table below, using factor 37:

Sample.	Percentage shells added.	Total shells found.	Percentage added shells found.
2A	4.55	10.56	33.12
2B	10.	15.6	8.2
2C	12.	15.7	8.3
7A	4.	13.0	5.6
7B	9.	12.5	5.1
7C	14.	19.1	11.7
12A	2.	9.9	2.5
12B	6.	16.3	8.9
12C	10.	21.5	14.1

Total shells found on the cocoa used for this experiment was 7.44 per cent. This value was deducted from total shells found in the above mixtures to give the value for added shells expressed in the last column.

DISCUSSION OF RESULTS.

It will be seen at a glance that the results are neither uniform nor accurate. This could well be expected, however, when the great variation in heavy constituents in the various grades of shells is considered. Goske examined seven samples and obtained the range of results cited above. The writers secured values which were uniformly higher than those shown

by Goske, the average of the same being practically what he obtained as the highest figure. Goske selects his highest value as the factor for calculation. In using this factor, results would be too low on cocoas to which shells having a lower percentage of heavy constituents were added, and would be too high for those samples to which cocoa shells having a higher percentage were added. The method, it appears to us, would be only approximately accurate where shells having practically that factor had been used. There is no way, however, of determining this point in the examination of any cocoa submitted to the analyst. In determining the accuracy of the method it appears more logical to select the average factor rather than the highest factor, although in the examination of commercial samples it is probably better to take the highest value obtained, because the benefit of the doubt is thereby given to the sample in each case. The table above shows lack of uniformity of results. Samples 12A, 12B and 12C contained shells, the factor of which was 52.20, much higher than the average selected for the calculation. In this case it would naturally be expected that the results would be too high. This, it will be seen, is the case. Samples 2A, 2B and 2C contained shells, the factor of which was 21.26, and in this case results would be expected to be too low. This expectation is realized. Samples 7A, 7B and 7C, however, contained shells, the factor of which was 36.66, practically the figure used in the calculations. Results are, in the three samples respectively, 1.6 per cent. high, 4.9 per cent. low, 2.3 per cent. low. If the highest shell value 52.20 had been used in the formula instead of 37, it will be seen that in the case of mixture 2A the amount of added shells indicated would have been 0, when in fact 4.5 per cent. of shells had actually been added to the cocoa. It would seem, therefore, that this method does not reliably indicate the addition of smaller quantities than 5 per cent. of cocoa shells and cannot be said to afford any accurate idea of the amount of husks actually placed in the commercial product.

Filsinger and Botticher found that the method of A. Goske gives low results.¹

U. S. FOOD & DRUG INSPECTION LABORATORY,
BUFFALO, N. Y.

THE ESTIMATION OF ESSENTIAL OILS.

By CHARLES D. HOWARD.

Received February 10, 1911.

During 1908 the writer published a method² for the determination of essential oils in extracts and pharmaceutical preparations, involving precipitation and extraction in a Babcock milk bottle, the small quantities of chloroform and ether used being volatilized by rapid evaporation in a water bath. This method was applied to a variety of extracts, including, incidentally, benzaldehyde, although there was no intent to claim that it afforded results of any value in the latter in-

stance.³ The method was subsequently criticized by Hortvet and West,² the authors claiming that the procedure did not serve to eliminate all of the chloroform and that extraction was not complete.

As a result of further experience, it is admitted that this method sometimes affords erratic results in the case of certain oils and that the average worker is liable to encounter some difficulty in securing concordant and accurate figures. It has proved of value, however, in the case of such oils as lemon, orange, wintergreen and peppermint. A method of this character has the advantages of being simple and quickly carried out, requires no large quantity of solvent, and avoids the difficulties in connection with drying and weighing the oil—the latter, in our experience, proving not inconsiderable.

Based upon the conviction of the writer that a much smaller quantity of solvent than that prescribed by Hortvet and West can be made to serve for complete extraction, the following modification was devised and has been used in this laboratory during the past year with good results, having been applied to most varieties of essential oil preparations. The procedure involves application of the principle, referred to by the writer in his original paper and since confirmed by Hortvet and West,³ that when an ethereal solution of an essential oil is *rapidly* evaporated, no appreciable loss of oil occurs.

Procedure.—Transfer 20 cc. of the extract to a four-ounce separatory funnel; in the case of preparations containing more than five per cent of oil, take but 10 cc. Add 50 cc. of water and (except in the case of oils of the type of cinnamon and clove) two drops of strong hydrochloric acid. Shake out with three portions of ether, using 15 cc., 10 cc. and 5 cc. After each extraction except the last, the ether solution may be run out into a small flask, which is kept stoppered if a series of determinations is being run simultaneously. The combined ether extracts are washed once with 10 cc. of ether-saturated water for removal of the bulk of the alcohol, then cautiously transferred to a 10 per cent. milk bottle, rinsing the flask and tip of the funnel with an additional two or three cc. of ether. Attach a bulb tube to the stem of the bottle and connect with a filter-pump, immerse the bottle in nearly boiling water, start the pump and shake with a gentle rotary motion at first. When all danger of spiring has passed, shake *violently* and toward the last immerse in boiling water for a few seconds, or until the application of a match flame demonstrates the complete elimination of the ether. The removal of most of the latter should require not more than two or three minutes. Finally add cold water and centrifuge. In the case of oils heavier than water, salt solution must be used as the floating agent, except with wintergreen, for which cold sulphuric acid (1:2) may be safely and most conveniently used.

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CONCORD, N. H.

¹ *Z. öfentl. Chem.*, **16**, 311.

² *Jour. Am. Chem. Soc.*, **30**, 608 (1908).

³ *Loc. cit.*, pp. 608, 610.

² *This Journal*, **1**, 84 (1909).

³ *Loc. cit.*, p. 88.

REPORT ON METHOD OF DETERMINATION OF GLYCEROL.

By EUGENE PROBECK.

For some time chemists have failed to agree upon a standard method for the determination of glycerol. As the two methods most in use, the acetin and the bichromate, are fully described in many text-books, it is unnecessary to repeat them.

In the bichromate method, I did not remove the chlorine and albuminous matter as recommended by many chemists but found it more advantageous to make a correction for these impurities by means of a blank test. This blank test depends upon the volatility of glycerol below 160°C ., leaving behind the salts, polyglycerols, albuminous matter and other organic impurities which do not volatilize.

Preliminary Test.—I weighed out about 2 grams of the sample, diluted it to 200 cc. and tested 20 cc. of it for acidity, using phenolphthalein as an indicator. I found it took 2 drops of $N/2$ sodium hydroxide to neutralize the 20 cc. I added 2 drops to each 20 cc. I used for analysis and also added 2 drops to each 0.2 gram of glycerine used for the blank test. The purpose of using an alkaline solution is to prevent any volatile acid from escaping by converting it into its sodium salt. If the glycerine is not neutralized in the blank test, the effect of the volatile acids on the bichromate solution cannot be determined.

The so-called blank test is made by evaporating about 0.2 gram of neutralized glycerine on a watch glass at 160°C . in a manner similar to the carbonaceous test given by Lewkowitsch in his "Technology of Fats, Oils and Waxes." The residue is oxidized with the bichromate solution at the same time that the glycerine is. To prevent overheating and be certain of complete oxidation, both the residue and glycerine are heated on the same water bath from $1\frac{1}{2}$ to 2 hours. The number of cc. of bichromate solution used to oxidize the residue is deducted from the number of cc. used for the sample and from the difference, the per cent. of glycerol is calculated. The blank test makes a correction for all impurities likely to be present except volatile monohydric and dihydric alcohols and volatile aldehydes, chiefly acrolein.

I tested the glycerine with an ammoniacal silver nitrate solution but no silver mirror appeared, proving absence of aldehyde. If aldehydes are present, they must be removed, or the acetin method must be used. Experiments were made to find out the conditions under which acrolein is formed. I heated some crude glycerine to 160°C . as quickly as possible and then to 200°C . and no odor of acrolein was noticeable.

Carbonaceous tests have also been made to find out first, the effect of temperature on the glycerine and second, the effect of sodium chloride on glycerine when heated. For convenience and clearness, it is well to divide the work into five parts:

I. Two carbonaceous tests were made of the crude glycerine with these results: first trial 5.45 per cent., second trial 5.50 per cent.

II. A 100 cc. Florence flask was nearly filled with crude glycerine and heated as quickly as possible in

an oven to 160°C . The glycerine was kept at this temperature for one hour and then two carbonaceous tests were made with these results: first trial 5.50 per cent., second trial 5.55 per cent.

III. The Florence flask was refilled with fresh glycerine, heated as quickly as possible to 200°C . and was kept at this temperature two hours. The carbonaceous tests made with this glycerine gave nearly the same results as in the first two cases, indicating that the glycerine can be heated to 200°C . without polymerization or decomposition. The results were: first trial 5.54 per cent., second trial 5.60 per cent.

IV. A fresh portion of glycerine was treated in the same manner as above except that the temperature was raised as quickly as possible to 250°C . and kept at 250°C . for two hours. The carbonaceous tests gave much higher results, as shown. First trial 12.60 per cent., second trial 12.50 per cent. These results indicate that glycerine cannot be heated to 250°C . without decomposition, polymerization, or both.

V. Another Florence flask was nearly filled with crude glycerine and considerable sodium chloride was added. The glycerine was treated in the same way as in IV. The carbonaceous tests gave these results: first trial 8.80 per cent., second trial 9.01 per cent. The presence of salt in this case seems to retard the formation of polyglycerols. Sodium chloride was used because it occurs in soap lye glycerine and it has been claimed that salts in glycerine interfere with the bichromate method.

The object of making so many carbonaceous tests is to show that the blank test can be used to advantage in determining glycerol in both candle glycerine and soap-lye glycerine. In case volatile nonhydric and dihydric alcohols are present, both the acetin and bichromate methods are unreliable, as these alcohols are capable of being converted into acetyl compounds in the first method and capable of being oxidized in the second.

To show how accurate each method is, I made duplicate analyses of a crude glycerine with the following results:

	Acetin method. Per cent.	Bichromate method. Per cent.
First trial.....	86.08	86.93
Second trial.....	86.56	87.27
Average.....	86.32	87.10
Blank test correction.....		0.30
Corrected result.....		86.80

CONCLUSION.

From my experience with the acetin method, I conclude that no matter how carefully the method is carried out, the results are from 0.2 per cent. to 0.5 per cent. below the true value. The difficulty with the method is not on account of the impurities but on account of the manipulations introducing several sources of errors.

The bichromate method is preferable in the absence

of acrolein and other volatile aldehydes. If aldehydes are present, they must be removed before using the bichromate solution. A blank test simplifies the method and makes the result more accurate than by purifying the glycerine.

THE PRESENCE OF ARSENIC IN THE COATING OF TABLETS.

By H. C. FULLER.

Received February 6, 1911.

While performing a systematic analysis of a certain proprietary remedy, a considerable quantity of arsenic was found and while ordinarily the presence of this substance, which is so commonly used in medicines, would call for little comment, in this particular instance the remedy was recommended for a disease where arsenic is not prescribed, though the remainder of the ingredients were those commonly used. This product was offered in the form of a chocolate-coated tablet and the analysis had shown that the "chocolate" was brown oxid of iron, and without going into the details of the preparation of iron oxid, it at once suggested itself that the oxid was contaminated with arsenic. On scraping off the coating from some of the tablets and submitting it to the Marsh test the source of the arsenic was apparent and none was subsequently found in the body of the tablet. Each tablet contained 0.000026 gram figured as As_2O_3 , about 1 part in 10,000, and if the patient took the quantity recommended he would consume daily $\frac{1}{7}$ the adult dose of As_2O_3 .

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THE DETECTION OF PRUNE JUICE AND CARAMEL IN VANILLA FLAVORING EXTRACTS.

By W. DENIS.

Received October 12, 1910.

The foreign coloring materials most frequently used in the preparation of factitious vanilla flavoring extracts are caramel, prune juice, and coal tar dyes.

The dyes are easily detected by the usual double dyeing tests, but the positive identification of caramel and of prune juice or mixture of the two offers greater difficulties.

The test for caramel most generally used in this country is probably the basic lead acetate test; by this method the dealcoholized extract is treated with a few cubic centimeters of basic lead acetate, when the following results are obtained:

1. With a pure vanilla extract a heavy pale brown precipitate is formed, while the supernatant liquid appears straw-colored or almost colorless.
2. With an entirely artificial extract prepared from synthetic vanillin and caramel, the addition of basic lead acetate may produce:
 - a. No precipitate.
 - b. A small amount of a dark brown precipitate leaving a dark brown supernatant liquid.
 - c. A heavy light brown precipitate and a straw-colored supernatant liquid, in other words a reaction absolutely identical with that given by a pure extract.

3. With extracts composed of 50 per cent. genuine vanilla extract and 50 per cent. of an extract prepared from synthetic vanillin and colored with caramel precipitates of varying density and shade are obtained, the color and volume of the precipitate depending in a large measure on the amount of vanillin present.

While engaged in the laboratories of the U. S. Bureau of Chemistry in the examination of several hundred samples of commercial vanilla extracts the author had ample opportunity for judging of the efficiency of this test, which after many trials appears to her to be practically worthless, and frequently misleading when employed in the form at present given in the official methods of the Association of Official Agricultural Chemists.¹

About two years ago the fact that vanillin in 0.4 per cent. solution gives a copious precipitate with basic lead acetate was brought to my notice by Mr. A. V. H. Maurey.

This fact at once explains the anomalous results frequently obtained when attempting to apply the lead acetate test to commercial extracts which contain absolutely no resins and show no color soluble in amyl alcohol or in ether; this class of extracts have usually a high vanillin content, 0.25 per cent. to 0.50 per cent., so that, when to the dealcoholized extract, we add basic lead acetate a copious precipitate is formed which carries the caramel down with it, giving finally a pale brown precipitate and an almost colorless supernatant liquid, exactly the result obtained with a pure extract.

To test the accuracy of this conclusion artificial extracts were prepared in the laboratory containing respectively 0.10 per cent., 0.20 per cent., 0.30 per cent. and 0.40 per cent. vanillin dissolved in 10 per cent. alcohol and colored with caramel.

On the addition of basic lead acetate solution to these extracts practically no precipitate was obtained with the one containing only 0.10 per cent. vanillin. With the three more concentrated solutions large precipitates were obtained which in the case of the one containing 0.4 per cent. vanillin was sufficiently copious to carry down with it practically all the caramel. The following modification of the lead acetate test has therefore been devised and has been extended to include the detection of prune juice.

To 25 cc. vanilla extract contained in a 100 cc. beaker add 50 cc. water and evaporate on a steam bath to a volume of 20 cc., filter off the precipitated resins and wash the filter with about 5 cc. water, the washings being allowed to mix with the filtrate. When cold, place in a small separatory funnel and extract twice with two 15 cc. portions of ether; the color of the first ether extract should always be noted; the coloring matter of the vanilla bean is fairly soluble in ether, caramel and prune juice are absolutely insoluble.

Now draw off the aqueous liquid into a beaker and warm for a few minutes on the steam bath to get rid of the last traces of ether, cool, place in a 100 cc. graduated cylinder and add 1 cc. basic lead acetate of specific gravity 1.25, mix by inverting the cylinder two

¹ U. S. Bur. of Chem., *Bull.* 107 (revised).

or three times and let stand until the precipitate settles.

If caramel be present the precipitate will be dark brown in color, while the supernatant liquid will be dark colored also. After the color of the precipitate and liquid have been observed, add 5 cc. glacial acetic acid and shake; in the presence of a pure extract, or, of an extract colored with caramel, the precipitate

the eighth edition of the U. S. Pharmacopeia; the prune juice was prepared by extracting dried California prunes with 70 per cent. and with 30 per cent. alcohol, the Sherry color was made by evaporating down on the steam bath a pure California Sherry to $\frac{1}{10}$ of its original volume.

Below is given in tabular form the results obtained

Color of precipitate with basic lead acetate.	Color of supernatant liquid when precipitate settles.	Action on addition of glacial acetic acid to lead acetate ppt	Appearance of the ethereal layer.	Quantity of resins.	Indicates.
None	Dark brown	All dissolves	No color	None	An entirely artificial extract colored with caramel.
Dark brown	Colorless	Gelatinous reddish brown residue	No color	None	An entirely artificial extract colored with prune juice.
Dark brown	Brown	Gelatinous reddish brown ppt.	No color	None	An entirely artificial extract colored with prune juice and caramel.
Dark brown	Brown	Gelatinous reddish brown ppt.	Small amt. color	Small quantity	An extract containing some natural vanilla color together with caramel and prune juice.
Voluminous, light colored	Colorless	Quan. of colorless ppt. undissolved	Fair amt. color	Small	An extract containing some natural vanilla color together with sherry residues.
Voluminous, light colored	Colorless	All dissolves	Much color	Large	A straight vanilla extract.
Voluminous, light colored	Colorless	All dissolves	Much color	None	Is probably an extract made by extracting the beans with glycerine

will immediately dissolve. If prune juice has been used, there will be obtained, on the addition of basic lead acetate to the extract after removal of alcohol, resins and vanillin in the manner above described a very voluminous dark colored precipitate, while the supernatant liquid will be almost or entirely colorless. On addition of 5 cc. glacial acetic acid to this precipitate it will be found that there is present a lead salt insoluble in acetic acid. This insoluble substance is of a gelatinous reddish brown appearance much resembling the precipitate of ferric hydroxid.

The following precautions are necessary in applying the test:

1. The coloring matter of Sherry wine is said to be sometimes used to color and flavor vanilla extract. This vehicle gives with basic lead acetate a copious light colored precipitate closely resembling in appearance, the precipitate produced under like conditions from a pure vanilla extract but differing from the latter in containing a body insoluble in acetic acid, which body is left as a light flocculent precipitate after treatment of the lead acetate precipitate with this acid. If, however, a mixture of Sherry and caramel have been used, this precipitate will be colored brown and is thus very difficult to distinguish from a mixture of caramel and prune juice.

2. The observation as to whether or not acetic acid has dissolved all of the precipitate produced by basic lead acetate should be made immediately after adding the acid, as on standing for several hours or over night, traces of such precipitate begin to appear when extracts of known purity are under examination. We have found that the extraction with ether described above apparently does not remove from a pure extract any lead-precipitating substance except the vanillin so that with such a product after extraction with ether, there is obtained, on the addition of basic lead acetate, a copious very light colored precipitate.

The pure vanilla extract used in working out the above method was prepared from a medium grade of Bourbon beans according to the directions given in

in the examination of various pure and artificial extracts by the above method.

METHOD FOR NICKEL-ZINC SEPARATION IN GERMAN SILVER AND OTHER ALLOYS.

By LA VERNE W. SPRING.

Received February 27, 1911.

The nickel-zinc separation has always been a serious matter for the chemist who had to do it only occasionally and nearly as forbidding for him who was so unfortunate as to encounter it regularly. It was one of those things from which he was praying to be spared, but which he felt he could sometimes do little to avoid.

Some of the modifications of the sulphide separation can be made to work but it is no method for a busy laboratory or for inexperienced hands. The fixed alkali hydroxide method is open to objections. The titration of the nickel with potassium cyanide in the presence of sodium pyrophosphate works at least approximately under the proper restrictions, but does not allow of a direct determination of the zinc.

Since the announcement during the past three or four years of the German methods for direct precipitation of nickel as nickel glyoxime or as nickel dicyandiamidine from solutions of almost any other metals, our own troubles have ceased quite completely. The analysis of German silver means now little more than analysis of a brass and the new methods could be used advantageously by many more chemists than appear to be using them. I do not claim originality in the method as used in our laboratory for the past two years, for though I do not know that certain parts of the method have ever been published, they have, in a way, been forecast by the German chemists, Grossmann, Brunck, *et al.*, in articles in the German chemical magazines. The method is as follows:

Weigh out one-half gram of the drillings, or more, according to the percentage of the constituents,

take out the tin with nitric acid, the lead as sulphate, copper by electrolysis and iron with ammonia as usual. Add five grams of ammonium chloride. Make the solution just neutral with hydrochloric acid, and add four-tenths of a gram of dimethylglyoxime dissolved in a little alcohol for every tenth of a gram of nickel supposed to be present. Add ammonia, drop by drop, until the solution smells slightly ammoniacal. Let stand just below the boiling point for one-half hour (more or less according as the nickel separates completely). Filter hot through counterpoised filters or on a weighed gooch, wash with hot water and dry in the air bath at 105° C. to constant weight. Weigh and calculate the nickel.



Until a little experience has been acquired, the filtrate should be tested to make sure that no nickel has escaped precipitation. Add 0.05 gram more of the dimethylglyoxime in a little alcohol, see that the solution is just ammoniacal and let stand for a few minutes. There should be no reddening of the solution, which would mean more nickel. Make the filtrate just acid with concentrated hydrochloric acid and add an excess of ten cubic centimeters. Boil for ten minutes to break up the dimethylglyoxime in the solution, add ten grams of microcosmic salt dissolved in a little water, neutralize with ammonia and hydrochloric or acetic acid until the solution neither turns blue litmus paper red nor red paper blue, and let stand just below the boiling point (do not let bump) until the precipitate has become granular. Filter under suction, wash with hot water, ignite in a weighed porcelain crucible, cool and weigh as zinc pyrophosphate. $\text{Zn}_2\text{P}_2\text{O}_7 \times 0.42913 = \text{Zn}.$

Dimethylglyoxime can be bought for \$2.50 per ounce.

CRANE COMPANY LABORATORY, CHICAGO.

A RAPID VOLUMETRIC METHOD OF SUGAR ESTIMATION.

By W. F. SUTHERST.

Received February 14, 1911.

While carrying out a number of sugar estimations in citrus fruits, at the Experiment Station of the Bonita Union High School, Lordsburg, Cal., an immense amount of time seemed to be taken up in finding the point when all the Fehling solution was reduced. The writer adopted the following method:

Fifty cc. of normal Fehling solution were heated to boiling in a porcelain casserole, and the trial sugar solution run in from a small burette or graduated pipette, till a faint blue color is apparent at the edge of the vessel. From this to the finish as further sugar is run in, a drop of the mixture is placed on the top side of a filter folded in half; the filtrate passes through, free from copper oxide, to the under side and the spot moistened with a drop of a solution containing 10 grams glacial acetic acid, 1 gram potassium ferrocyanide in 100 cc. water. On holding up to the light the faintest trace of copper ferrocyanide can be perceived, and the end of the reaction plainly indicated at the first trial.

THE IMPORTANCE OF A STANDARD TEMPERATURE FOR SPECIFIC GRAVITY DETERMINATIONS, AND FOR STANDARDIZING MEASURES OF CAPACITY.¹

By G. W. THOMPSON.

Received February 11, 1911.

Chemists generally appreciate the advantage of the metric system of weights and measures. Weights and measures in this system are related so simply that the terms, in many practical cases, become interconvertible.

In this country, where the old system of weights and measures prevail, the common measure of capacity is the gallon. The Bureau of Standards and its antecedents adopted the temperature of the maximum density of water as that at which gallon measures should be standardized. A gallon is 231 inches. A great many materials, such as oils and prepared paints, are sold by measure. In very many cases these materials have values dependent on measure. Thus, in the case of raw linseed oil, commercially a gallon weighs 7.50 pounds, although the actual weight is 7.75 pounds. Some purchasers, however, insist on a gallon close to 7.75 pounds. The movement which is growing in strength for the sale of all commodities by accurate net weights and measures makes it very desirable that weights should be as far as possible convertible to measures.

On the other hand, there are probably cases where weights cannot so readily be determined as volume, in which case the ready conversion from volume to weight is a thing to be desired.

Considering these ends as of great commercial desirability, the question arises as to the best means to be used to bring them about. If specific gravity determinations were made at 4° C., it would be a simple matter to calculate the weight of a gallon at that temperature by multiplying that specific gravity by 8.336, the weight of a gallon of water in air. There are two difficulties, however, in the way of this procedure. One is that 4° C. is not a good temperature at which to make specific gravity determinations. Furthermore, with very few materials are their volume values fully measurable at that temperature. The volume value of a material should be measured at that temperature at which it is used.

Calculations have been made of the capacity of gallon measures at 20° C. standardized to contain 231 cubic inches at 4° C. It is found that such a copper measure contains at 20° C. 231.19 cubic inches and a similar brass measure 231.20 cubic inches. There are good reasons for basing our calculations at 20° C. although 25° C. has its advocates.

An important phase of this subject which should be considered is that most liquids expand with a higher coefficient of expansion than the materials from which measures are made. Commercially, therefore, the higher the temperature at which a material is measured, the less the weight will be. It might be considered a hardship to the consumer if a relatively high temperature should be adopted for measuring liquids,

¹ Read at the meeting of the Industrial Section of the American Chemical Society at Minneapolis, Dec. 28-31, 1910.

as the consumer would apparently receive less in pounds and it would appear as though the manufacturer would be correspondingly benefited. The benefit, on the other hand, which the consumer would derive from a standard temperature for measuring liquids, would ultimately be greater than any possible temporary loss he might sustain.

If we desire to calculate from specific gravity to weight per gallon, the question of ratio arises. Shall this specific gravity relate to water at the same temperature $\frac{t_m}{t_m}$ or shall it relate to water at $4^\circ \text{C. } \frac{t_m}{4^\circ \text{C.}}$? Practically it does not make any difference, however, as we will show by the following reasoning:

- 1 The gallon is 231 cubic inches.
- 2 A brass gallon measure standardized at 4°C. contains 231.20 cubic inches at 20°C.
- 3 a, 231.20 cubic inches of water at 4°C. weighs in air 8.3432 lbs. = W.
- b, 231.20 cubic inches of water at 20°C. weighs in air 8.3285 lbs. = W_1 .
4. Specific gravity $\frac{20^\circ}{20^\circ}$: Specific gravity $\frac{20^\circ}{4^\circ} =$
 $1 : 0.9982343 = W : W_1$

Therefore:

$$\text{Specific gravity } \frac{20^\circ}{4^\circ} \times W = \text{specific gravity } \frac{20^\circ}{20^\circ} \times W_1.$$

For practical purposes, therefore, we could define the gallon in about the following terms:

"The gallon of liquid shall be considered as equal to the weight obtained by multiplying a, the specific gravity of the liquid at $\frac{20^\circ \text{C.}}{4^\circ \text{C.}}$, by 8.3432 lbs. or b, the specific gravity of the liquid at $\frac{20^\circ \text{C.}}{20^\circ \text{C.}}$, by 8.3285."

Whether this definition would be of practical value in specifications or not is yet to be determined, but it is certain that it at least is deserving of consideration.

A METHOD FOR THE DETERMINATION OF TIN IN CANNED FOODS.

By HERMAN SCHREIBER AND W. C. TABER.

Received January 27, 1911.

The determination of tin in canned foods, which has recently become of increased importance, may be made by several methods, each having its advantages and defects. Ashing the material at a very low heat in a muffle will give correct results with some foods under some circumstances, but not always, and when the composition of the material is not known, it is not safe to apply this method. Moreover, tin and its salts are volatilized by heat in the presence of chlorid of ammonia and probably with other chlorids also, since it is well known that sodium chlorid volatilizes on heating strongly. When small amounts of a metal are to be recovered from a large amount of organic matter, the danger of mechanical loss in the fumes is very great. After ashing, the ash must be fused with caustic alkali if all of the tin is to be recovered, so that this process does not offer any advantage over the

method herein proposed in regard to the time necessary for making the determination.

Munson¹ has proposed carbonizing the organic matter with sulphuric acid and heat, and ashing in a muffle with the aid of nitric acid. Determinations made by this method did not give satisfactory duplicates, and the results represented only about 50 per cent. of the tin present, as determined by sulphuric acid digestion (Table I) in Halenke's wet ashing method, as modified by Schryver.² In this method the organic matter is destroyed by digestion with large amounts of sulphuric acid with the aid of potassium sulphate.

TABLE I.
COMPARISON OF THE MUNSON METHOD AND THE SULPHURIC ACID OR WET COMBUSTION METHOD (SCHRYVER).

Sample.	Gram of tin found in 50 grams of sample.	
	By Munson method	By sulphuric acid method (Schryver)
Herring in tomato sauce.....	0.0236	0.0458
Do.....	0.0217	0.0652
Sardines.....	{ 0.0318 } { 0.0462 }	0.0652
Do.....	{ 0.0682 ³ } { 0.0801 ³ }

Table II shows that the results obtained when the precipitates are weighed as stannic oxid (SnO_2) are as correct as when the precipitate is dissolved and determined electrolytically⁴ as tin. Schryver has shown that the wet combustion method gives accurate results and good duplicates. This is also shown by the determinations given in Table II. However, this method has some very serious practical defects. When tin is to be determined in meat, fish, or sirups, only 25 grams of material can be digested in one flask. This necessitates making two digestions in order that an amount can be used which will avoid the great multiplication of the analytical error which would occur if the result were calculated as milligrams per kilogram. Using such small quantities of the sample increases the error of weighing and sampling, and, moreover, limits the amount of work which can be done under ordinary conditions. The flasks have a tendency to break during the digestion, which, together with the foaming of the material, requires constant attention and considerable experience before satisfactory results can be obtained. No attempt was made to determine the amount of tin which could be recovered by the various methods by adding known amounts of soluble tin salts to food, since this would not give conditions analogous to those met in practice.

Our work indicated that the following was the most satisfactory method of making a sulphuric acid digestion: Weigh 25 grams of fish or meat or 50 grams of vegetables into a beaker, wash into an 800 or 1000 cc. Kjeldahl flask, add from 100 to 150 cc. of water, 25 grams of potassium sulphate, 50 cc. of sulphuric acid (sp. gr. 1.84), and a few glass beads. Place over a small flame, rotate a few times till it boils, then in-

¹ U. S. Dept. Agr., Bur. of Chem., *Bull.* 107, 62 (revised).

² Report 7 of the Local Government Board (medical department) of Great Britain on the presence of tin in certain canned goods.

³ Wet combustion not made, given to show poor concordance of results.

⁴ U. S. Dept. Agr., Bur. of Chem., *Bull.* 207, 69 (revised).

crease heat and boil vigorously until the water is boiled off and fumes of sulphur trioxid appear in the neck of the flask and settle back, remove it from the flame before it foams or caking will ensue and the flask break in subsequent boiling. Add 50 cc. of sulphuric acid (sp. gr. 1.84), turn the flame down so that it just touches the flask, and heat gently until the mass boils quietly. Again increase the heat and boil vigorously until decolorized. If the flask is placed in an asbestos ring, cracking can often be avoided. This digestion requires at least six hours.

TABLE II.

COMPARISON OF RESULTS BY WET COMBUSTION OR SULPHURIC ACID METHOD AND BY ELECTROLYSIS.

Gram of tin per 50 grams of sample.

Sample.	Wet combustion method. Gram.	Stannic oxid dissolved and redetermined by electrolysis. Gram.
Blackberry jam.....	{ 0.0126 } { 0.0128 }	0.0124
Herring.....	0.0325	0.0346
Herring in tomato sauce.....	0.0296	0.0304
Herring in bouillon.....	0.0464	0.0468

To determine the accuracy of duplicate determinations by the sulphuric acid method, samples of canned fish were very carefully prepared by passing them through a sausage grinder and then thoroughly mixing them by hand. From these mixtures duplicate weighings of 25 grams were made on an analytical balance to ± 0.05 gram and the following results were obtained:

TABLE III.

DUPLICATE DETERMINATIONS OF TIN BY THE SULPHURIC ACID OR WET COMBUSTION METHOD.

Sample.	Gram of tin in 25 grams of sample.
Composite fish:	
Sample A.....	{ 0.0134 } { 0.0138 }
Sample B.....	{ 0.0079 } { 0.0087 }
Sample C.....	{ 0.0164 } { 0.0158 }

To determine the effect of the presence of sodium chlorid on results obtained by the wet combustion method, 10 grams of salt were added to the material to be analyzed. The figures given in the following table prove that this had no effect on the results:

TABLE IV.

DETERMINATION OF TIN BY THE SULPHURIC ACID METHOD IN THE PRESENCE OF SALT.

Gram of tin in 50 grams of sample.

Sample.	50 grams of sample + 10 grams of salt.	Original sample.
Fish.....	0.0363	0.0339
Beets.....	0.0425	0.0419
Peas.....	0.0282	0.0254

If tin is to be estimated in foods, such as fish, which contain so great an amount of salt as not to be edible before soaking, it is better to determine the tin by the sulphuric acid method, as large amounts of salt would interfere with the burning off of the carbon by the

proposed method on page 259. However, such cases would be very rare, as salt fish are commonly packed in wood and not in tin.

The method proposed on page 259 requires practically no experience in its manipulation, and a large amount of the sample is used, in both of which points it is superior to the wet combustion method. It was at first thought that the destruction of the organic matter could be effected by an alkaline fusion, using alkaline hydrate and nitrates. However, when material, such as fish, which contains fat, is to be analyzed, it is impossible to make such a fusion, as it will burn and blow out of the crucible. When alkaline hydrates are used alone, a solid cake results which retards the complete destruction of carbon by coating the small particles. A mixture of hydrate, carbonate, and magnesium oxid was found to give a very porous fusion, in which the carbon was easily oxidized in the muffle. The fusion was at first attempted in large nickel crucibles with very good results as shown by Table V.

TABLE V.

COMPARISON OF THE SULPHURIC ACID OR WET COMBUSTION METHOD WITH ALKALI FUSION IN A NICKEL CRUCIBLE BY THE PROPOSED METHOD.

Gram of tin per 50 grams of sample.

Sample.	Wet combustion method.	Proposed method, using a nickel crucible.
Herring tomato sauce No. 3552.....	0.0397	{ 0.0400 } { 0.0383 }
Herring tomato sauce No. 3553.....	0.0325	{ 0.0351 } { 0.0334 }
Pineapple No. 4876.....	0.0102	{ 0.0110 } { 0.0101 }

The nickel crucibles, however, were very seriously attacked, and since they are expensive, it was thought that fusion in an iron crucible would be a great advantage on account of the lower cost and the higher melting point of iron. When iron crucibles were first substituted, the results obtained were lower than by the wet combustion method, and a repetition of the determination gave no solution of the difficulty. At this time hydrochloric acid was used for dissolving the fusions and finally, on the theory that the trouble was due to the solvent action of the iron chlorid on the tin, sulphuric acid was substituted for hydrochloric acid and correct results were obtained, as shown in Table VI.

TABLE VI.

COMPARISON OF RESULTS BY THE WET COMBUSTION METHOD AND THE PROPOSED METHOD USING DIFFERENT SOLVENTS AND AN IRON CRUCIBLE.

Gram of tin in 50 grams of sample.

Sample.	Wet combustion method.	Proposed method.	
		Using hydrochloric acid.	Using sulphuric and nitric acids.
Beets.....	0.0419	0.0331	{ 0.0416 } { 0.0403 } 0.0410
Tomatoes.....	0.0345	0.0290	{ 0.0331 } { 0.0310 } 0.0320
Peas.....	0.0254	0.0252	{ 0.0283 } { 0.0268 } 0.0276
Corn.....	0.0277	0.0238
Apples.....	0.0338	0.0239	{ 0.0320 } { 0.0343 } 0.0332
Spinach.....	0.0048	0.0060
Mushrooms.....	0.0107	0.0147
Canned fish.....	0.0325	{ 0.0298 } { 0.0328 } 0.0313

The results reported in Tables IV to VII were obtained in the preliminary work done in developing the proposed method. In the method, as then used, 5 grams of magnesium oxide were employed, and the solution of the fusion was not concentrated until it fumed with sulphuric acid, but was simply boiled down, and blue ribbon paper was used for the first filtration. It was found that the fusions could be burned at a lower temperature if 10 grams of magnesium oxide were used, which makes the burning much easier and materially lengthens the life of the crucible. It was also found best to use a larger amount of acid, as specified in the method, since under certain circumstances all of the tin was not dissolved when only 50 cc. of 1 : 1 sulphuric acid and 5 cc. of nitric acid were used. The use of blue ribbon paper was also abandoned, since it decreased the speed of filtration, and, furthermore, it has no apparent advantage (Table VII) when the precipitation is made as specified in the proposed method. The experimental data indicate that sulphuric acid alone will not take all of the tin into solution, although no explanation of this can be offered.

TABLE VII.

COMPARISON OF RESULTS BY THE WET COMBUSTION METHOD AND PROPOSED METHOD USING BLUE RIBBON FILTER PAPERS AND SULPHURIC ACID.

Gram of tin in 50 grams of sample.

Sample.	Wet combustion method.	Proposed method using blue ribbon filter papers ¹ for the first filtration and 50 cc. of 1 : 1 sulphuric acid and 5 cc. of nitric acid to dissolve the fusion.
Beets.....	0.0419	$\left\{ \begin{array}{l} 0.0403 \\ 0.0424 \end{array} \right\} 0.0414$
Peas.....	0.0254	$\left\{ \begin{array}{l} 0.0265 \\ 0.0275 \end{array} \right\} 0.0270$
Corn.....	0.0277	$\left\{ \begin{array}{l} 0.0269 \\ 0.0276 \end{array} \right\} 0.0273$
Apples.....	0.0338	$\left\{ \begin{array}{l} 0.0303 \\ 0.0329 \end{array} \right\} 0.0323$
Fish.....	0.0325	$\left\{ \begin{array}{l} 0.0303 \\ 0.0329 \end{array} \right\} 0.0316$

The proposed method has several advantages over the wet combustion method: (1) it decreases the errors of sampling; (2) it decreases the errors due to multiplication when calculating to milligrams per kilogram; (3) there need be no loss of samples if the material is properly ground and not heated too rapidly on the hot plate; (4) in the wet ashing methods it is necessary to neutralize a large amount of acid before precipitating with hydrogen sulphide.

Molasses and heavy syrups must be dried longer on the hot plate than any other material analyzed, over three hours being necessary to dry these properly. However, as it requires no attention at this stage, this is not a serious defect as compared with the difficulties of determining tin by the wet ashing method. In drying any material on the hot plate it is not necessary to dry it down to a hard crust if it is put in a cold muffle and heat applied gradually. If tin is to be determined in oils, less of the sample should be used, so that there will be an excess of free sodium hydrate.

¹ These tin oxides were only very slightly discolored, being very nearly the same shade as those from the wet combustion.

The sulphuric acid method for the determination of tin can not be applied to oils, and therefore no comparison of the two methods can be made.

THE PROPOSED ALKALI FUSION METHOD.

Pass the sample through a meat-grinding machine and mix the resulting mass well so as to get as homogeneous a sample as possible. Weigh 100 grams of the sample and 10 grams of magnesium oxide into an 8-ounce wrought-iron crucible on a rough balance. Add 50 cc. of an aqueous solution containing 150 grams of sodium hydrate and 100 grams of sodium carbonate per liter, stir well with a short piece of stout glass rod, add 75 cc. of 95 per cent. alcohol and stir again. Place on the steam bath and evaporate the alcohol. This must be done with care, stirring frequently at the beginning, else it may bump or foam over, but if the material is gradually heated there is no danger of loss. If the material foams, remove from the steam bath or hot plate for a moment, and then replace on the bath and it will usually boil quietly. Large lumps in the mass will cause bumping, therefore the sample should be as fine as possible. Fish liquefy on the steam bath, boil down quietly, and without bumping. After danger from frothing has ceased, apply the full heat of the steam bath. This evaporation requires about one hour. Transfer to a hot plate covered with a thin sheet of asbestos and dry down gradually, running at from 130° to 160° C. at first (determine temperature by laying a thermometer on the asbestos); then raise the temperature and continue the boiling, finally using the full heat of the hot plate, which should be sufficient to boil off sulphuric acid. This requires from one and a half to two hours. Place in a cold muffle, heat gradually until all volatile matter is driven off, and then burn until all of the carbon is destroyed. This requires from two to three hours. Remove from the muffle as soon as burned, cool, cover the residue with water, and let stand a few minutes. Using an iron spatula, scrape and wash the contents of the crucible into a 600 cc. beaker. Cover the beaker and add gradually 40 cc. of dilute sulphuric acid (1 : 1) and 10 cc. to the crucible containing some water. Rotate, scrape the sides of the crucible with a spatula, and wash into the beaker. When the reaction is ended, add 50 cc. of sulphuric acid (sp. gr. 1.84) and 30 cc. of nitric acid (sp. gr. 1.42). Cover with a watch glass and boil briskly on a hot plate, finally with the full heat of the hot plate, until the residue gives off fumes of SO₃. Allow to fume for 10 minutes, remove from the hot plate and allow to cool but not to solidify. Pass the stem of a funnel bent at an angle over the lip of the beaker and under the cover glass and add successively small amounts of distilled water through the funnel from a wash bottle until violent action has ceased. Then add rapidly about 150 to 200 cc. more water through the funnel and remove the funnel and watch glass, washing into the beaker with distilled water. Stir the cake in the beaker and wash into a 1-liter erlenmeyer with distilled water.

The total volume in the erlenmeyer at this time

should be about 300 to 400 cc. Cool, pass in hydrogen sulphid for a few seconds, rotate the flask and add 28 per cent. ammonium hydroxide slowly until the black color of the precipitated iron sulphide just persists on rotating the flask. Immediately make acid with 1 : 1 sulphuric acid and add 10 cc. excess of the dilute acid. Dilute the contents of the flask to 1 liter with boiling water and continue passing in a rapid stream of hydrogen sulphid for 25 minutes more, cork, and let stand over night. The next morning heat on the steam bath for about half an hour, rotating the flask two or three times during the heating, partly cool by setting in cold water, so that the flask can be handled easily, and filter onto a 12.5 cm. ashless white ribbon paper, No. 589, washing the filter with a solution consisting of 50 cc. glacial acetic acid and 100 cc. of a saturated solution of ammonium acetate, made up to a liter with distilled water. Wash the precipitate six times with this solution, filling the filter at each washing. Return the filter paper and precipitate to the erlenmeyer, add 100 cc. of 20 per cent. potassium hydroxid and boil over a free flame for a couple of minutes until the filter paper is broken up and the solution is clear. (The flask can be manipulated over the flame easily with a large wooden test-tube holder made of strips of pine wood and rubber bands.) Immediately decant through a double white ribbon filter paper of 12.5 cm. into a 400 cc. beaker, washing the flask and filter with successive portions of hot water until the filtrate comes through colorless. The filtrate will have a volume of about 200 to 300 cc. Add 20 cc. of concentrated hydrochloric acid to this solution, stir, add a few drops of phenolphthalein and add concentrated hydrochloric acid from a burette until the dark color of the solution disappears, then add 1 cc. excess of the acid. Test with a strip of litmus and see that the solution is acid, stir well, place on a steam bath, heat for 20 minutes, cover, and let stand over night.

In the morning test the supernatant liquor, which should be perfectly clear and brilliant, with a piece of blue litmus. If not acid, make so with concentrated hydrochloric acid and then add an excess of 1 cc. If the supernatant liquor is acid and turbid, make alkaline with potassium hydroxide and then acid with 1 cc. excess. The solution must be neither alkaline nor too acid, or there will be trouble in filtering and washing. Heat on a steam bath for half an hour, stirring two or three times. Filter onto a 12.5 cm. white ribbon paper. The precipitate will sometimes run through and must be returned until the filtrate is perfectly clear and brilliant. If the solution to be filtered is stirred vigorously, allowed to stand until the precipitate clots, and then poured onto the filter, refiltering may usually be avoided. The filtrate must be perfectly clear or some tin will be lost. Wash alternately with distilled water and the ammonium acetate solution previously mentioned until the filtrate obtained from a washing with distilled water is free from chlorides. (Do not mistake the precipitate given by the acetate solution and silver

nitrate, which is soluble in water, for silver chloride.) This requires washing until the volume of the filtrate is 200 cc. or more. Fill the filter at each washing. Place the moist filter in a porcelain crucible, dry and char on an asbestos gauze, and burn off all carbon over the free flame. Cool in a desiccator and weigh as stannic oxide.

Table VIII gives a comparison of the results obtained by this method and those obtained by Schryver's method.

TABLE VIII.
COMPARISON OF PROPOSED METHOD WITH SCHRYVER'S SULPHURIC ACID METHOD.

Gram of tin in 100 grams of sample.		
Sample.	Proposed alkali fusion method.	Schryver's sulphuric acid method.
Mushrooms.....	* { 0.0385 } { 0.0366 } { 0.0355 }	0.0368 0.0370
Herring in tomato sauce.....	0.0682 ¹	0.0664
Apples.....	0.0700 ¹	0.0676
Beets.....	{ 0.0859 } { 0.0847 }	0.0853 0.0838
Tomatoes.....	{ 0.0662 } { 0.0697 }	0.0679 0.0698
Do.....	0.0210 ¹	0.0204
Herring in bouillon.....	0.0959 ¹	0.1008
Kippered herring.....	{ 0.0336 } { 0.0299 }	0.0317 0.0320
Composite samples of fish:		
Sample A.....	0.0508 ¹	0.0544
Sample B.....	{ 0.0338 } { 0.0386 }	0.0363 0.0332
Sample C.....	{ 0.0615 } { 0.0638 }	0.0627 0.0644

Experiments were made to determine the relative value of potassium hydrate and ammonium sulphid as solvents for tin sulphid and it was found that they gave concordant results. In one instance the solution by potassium hydrate gave 0.0313 gram of stannic oxid, and the ammonium sulphid gave 0.0318 gram. The sample of ketchup on which these determinations were made contained a large amount of sand, and the results show that there is no danger of silica contaminating the stannic oxid when potassium hydroxid is used. Copper was found in some of the foods examined, and since copper sulphid is more soluble in ammonium sulphide than in potassium hydrate, it seemed advisable to use the latter.

A muffle 9 by 21 inches will hold 10 crucibles at a time, and one analyst can easily make 20 determinations in a week. If the heating in the muffle is gradual and the crucibles are removed as soon as all of the carbon is destroyed, the crucible will not be blistered on the outside and only slightly on the inside, and can be used for repeated fusions. If the crucibles have been spun with a copper or brass tool, the traces of copper adhering to the crucible should be filed off. Fifteen determinations can be weighed, dried, and burned in nine hours, using a hot plate 14 by 18 inches, and a muffle 9 by 21 inches. This requires three hours' continuous watching, and then only an occasional inspection of the muffle and changing the position of the crucibles. Straight ashing, on the other hand, requires at least seven hours' burning in the muffle if even approximately accurate results

¹ Duplicates not run, as there was not sufficient material left.

are to be obtained and if the food can be put into the muffle without previous drying.

Two hundred and fifty determinations were made in working out the details of this proposed method.

SCIENTIFIC SOCIETIES.

DEDICATION OF THE CHEMISTS' CLUB.

The formal dedication of the New Chemists' Club building was celebrated on March 17th to 19th by a series of scientific meetings and social functions participated in by a large number of prominent scientific men and members of the American Chemical Society, Society of Chemical Industry, and American Electrochemical Society.

PROGRAM

Dedication Exercises

Friday afternoon, March seventeenth

Address—Dr. Morris Loeb, President of the Chemists' Building Company.

Address—Dr. Edward S. Morley, Honorary President of the VIII International Congress of Applied Chemistry.

Address—Professor Alexander Smith, President of the American Chemical Society.

Address—Professor William Walker, President of the American Electrochemical Society.

Address—Professor Wilder D. Bancroft, on "Chemical Education."

Unveiling of Rumford Memorial by Professor F. W. Clarke.

Address—Dr. Russell W. Moore, President of the Chemists' Club.

Extraordinary Meeting American Chemical Society,

Friday Evening, March Seventeenth

Address—Professor Charles Baskerville, Chairman of the Section.

Illustrated Lecture—Professor R. B. Moore, "The Rare Gases of the Atmosphere."

Lecture—Professor Jacques Loeb, "The Characteristics of Living Matter from the Physico-Chemical Point of View."

Extraordinary Meeting American Electrochemical Society,

Saturday Morning, March Eighteenth

Address—Mr. Elmer A. Sperry, Chairman of the Section.

Lecture—Dr. W. R. Whitney, "Mental Catalysis."

Lecture—Professor Wilder D. Bancroft, "Chemistry of Phosphorescence."

Extraordinary Meeting Society of Chemical Industry,

Saturday Afternoon, March Eighteenth

Address—Dr. Charles F. McKenna, Chairman.

Lecture—Dr. Wm. P. Mason, "The Contributions of Chemistry to Sanitation."

Lecture—Professor Charles F. Chandler, "The History of Chemical Industry in New York City."

First Banquet in the New Building.

Saturday Evening, March Eighteenth

Toastmaster

President Russell W. Moore

Master of the Revels

Mr. Elwood Hendrick

Concert under the Auspices of the Chemists' Club,

Sunday Afternoon, March Nineteenth

GENERAL MEETING OF AMERICAN ELECTROCHEMICAL SOCIETY.

APRIL 6TH TO 8TH.

NEW CHEMISTS' CLUB BUILDING, NEW YORK.

PROGRAM

THURSDAY, APRIL 6TH

10.00 A.M. *Annual Business Meeting* of the Society, in the Assembly Hall of the Chemists' Club. Reports of Board of Directors; Announcement of the Annual Election.

PAPERS.

Report of the Committee on Standard Tests for Dry Cells: C. F. BURGESS.

Electrically Fused Alumina as a Refractory: L. E. SAUNDERS.

A New Electric Resistance Furnace: F. A. J. FITZGERALD.

A New Laboratory Electric Furnace: M. M. KOHN.

The Johnson Electric Zinc Furnace: J. W. RICHARDS.

The Condensation of Zinc from Electric Furnaces: F. T. SNYDER.

Reliability of Electric Furnaces for Commercial Work: F. T. SNYDER.

2.00 P.M. *Visit to the Laurel Hill Works of the Nichols Copper Co.*

7.00 P.M. *Subscription Dinner, en famille, at the Chemists' Club.*

FRIDAY, APRIL 7TH

9.30 A.M. PAPERS.

The Electric Cyanamid Process for Treating Gold Ores: J. F. CLANCY.

The Electrolytic System of Amalgamating Gold Ores: E. E. CAREY.

The Electrolytic Corrosion of Electroplated Objects: W. S. LANDIS.

Electrolytic Refining as a Step in the Production of Steel: C. F. BURGESS.

Some Problems of the Electroplater: G. B. HOGABOOM.

The Haas-Oettel Electrolytic Cell: E. E. NISWONGER.

Electrical Heating for Preventing Superheating of Liquids: J. HOWARD MATHEWS.

A Mercurous Perchlorate Coulometer—Preliminary Experiments: F. C. MATHERS.

Exhibition of the Schoenherr Arc for Fixing Atmospheric Nitrogen: J. W. TURRENTINE.

Electric Discharges in Gases: L. A. PARSONS.

The Mechanism of Electrolytic Transfer: J. W. RICHARDS.

AMERICAN SOCIETY OF MECHANICAL ENGINEERS.

The sixty-third meeting of the American Society of Mechanical Engineers will be held in Pittsburg, May 20th, to June 1st inclusive. The Society has not met in Pittsburg since 1884. Colonel E. D. Meier, of St. Louis, is President this year. There will be regular sessions for the reading and discussion of papers, and an inspection excursion through the leading industrial and manufacturing plants in and about Pittsburg.

AMERICAN MINING CONGRESS.

The Directors of the American Mining Congress, the permanent headquarters of which are in Denver, have selected Chicago as the meeting place for the 1911 session, which will be the 14th annual meeting of this body. The exact date has not yet been decided upon, but it will probably be sometime in October. The official call for the convention will be issued shortly, authorizing the appointment of delegates to the meeting by the President of the United States, governors of the various states and territories, the mayors of cities, and mining organizations, etc. It is probable that this will be the last annual session of the Mining Congress to which outside delegates

will be appointed, as the directors have for some time been working out plans which have in view the abolition of the delegate system, and permitting only members of the American Mining Congress to participate in the proceedings of the annual convention.

The Mining Congress is actively agitating the adoption of Workmen's Compensation laws by the various coal mining states with the object of providing a fund by a small tax on coal production, to furnish indemnity for the victims of mine disasters and a pension for aged mine workers. Recently a committee of the Mining Congress drew up a draft for a law of this character, which is now being submitted to the legislatures of many mining states for their consideration. The Mining Congress is also working for more efficient inspection and regulation of coal and metal mines with a view to decreasing the loss of life in mine disasters, the standardization of electric practice in mines, the general revision of the mineral land laws, etc.

These and other mining problems will be discussed at the Chicago meeting.

The 1911 meeting of the British Association will begin Aug. 30th. The president this year is Sir William Ramsay, and the chemistry section will be presided over by Prof. J. Walker.

An Institute for Research in Physical Chemistry has been founded in Berlin by Leopold Koppel, a well-known banker of that city. He has donated \$175,000 for the erection of the Institute and a further \$87,500 which will pay the running expenses for ten years.

NOTES AND CORRESPONDENCE.

EIGHTH INTERNATIONAL CONGRESS NEWS.

Dr. William H. Nichols, President of the Eighth International Congress of Applied Chemistry, was the guest of honor at a dinner tendered him by twenty-two members of the Executive and Sectional Executive Committees on Tuesday, March 7th, at the Engineers' Club, New York City. The occasion for this dinner was Dr. Nichols' departure on an extended European trip in the interests of the Congress.

Dr. Nichols' trip will no doubt be of the greatest benefit to the Congress and to American chemists. His travels will take him through Italy, Austria, Germany, France, Belgium, Holland and England, and he will personally carry the invitation of the American chemists to these countries to take part in the work and deliberations of the Eighth International Congress.

More than 9,000 copies of the Preliminary Announcement, dated March 6th, 1911, abstracted in the March JOURNAL, were distributed in the United States. Should any one interested in the Congress have been overlooked, a postal card to the Secretary of the Eighth International Congress of Applied Chemistry, 25 Broad Street, New York City, will bring one.

The Congress will not be ready to receive applications for membership until further notice.

A second pamphlet, ready for distribution in June, is in preparation and will give more detailed information about the preparation of the scientific activities of the Congress. It is the expectation that American manufacturers will see that their interests will be best served by earnest coöperation with their corresponding Sectional Committees and the preparation of appropriate scientific papers for presentation at the meetings of the Congress; it is in order that American manufacturers may have a better conception of the purposes and objects of the Congress and of the best ways of coöperation therewith that this second pamphlet is being prepared.

The Government of the Philippines has appointed Dr. Paul C. Freer, Director of the Bureau of Science, Manila, P. I., the Official Representative of the Philippines on the Organizing Committee of the Eighth Congress.

A NEW RUBBER TREE.

Professor John R. Allen, of Ann Arbor, has contributed an article to Mill Supplies of "A New Rubber Tree in Mexico," from which he favors us with a brief abstract.

The Pelo Colorado tree occurs on the Western slopes of the Sierra Madres Mountains in Mexico and so far

as known, this tree is found in no other locality. It is of the nettle family and when you touch the leaves or fruit it burns the hands. It will average about 6" in diameter to as large as 20" in diameter.

The tree is easily tapped and the sap runs freely. It has a pure white sap which looks a great deal like milk and which coagulates when exposed to the atmosphere for a short time. If water is sprinkled upon the sap as it leaves the tree it coagulates almost instantly.

We have tried the rubber in the factory and find it works very satisfactorily. We have made it into various articles of mechanical rubber and find it is easily manufactured into finished product. In every respect it seems entirely suitable for commercial purposes.

PROSPECTING FOR POTASH.

The United States Geological Survey has been instructed by Congress to prospect for deposits of potash salts in the United States, and \$20,000 has been appropriated for this purpose. This will imply the inauguration of prospecting by drilling, if any real progress is to be made, and such we believe is the intention of the Director of the Survey.

ANACONDA SMOKE DECISION.

The U. S. Circuit Court of Appeals of San Francisco has decided the Smelter Smoke case in favor of the Anaconda Company and against the farmers. The decision affirms that of Judge Hunt, of the Federal Court in Montana, although the farmers may appeal to the Supreme Court at Washington.

STEEL CORPORATION'S SHARE IN TOTAL OUTPUT OF IRON AND STEEL.

Wall Street Journal states that notwithstanding the hundreds of millions of dollars the United States Steel Corporation has spent for new construction and the acquisition of new properties, its relative position from the point of production of steel to the country's total output is not as strong as it was at the time of organization. The Steel Corporation has increased its capacity in the neighborhood of 75 per cent. since organization, but its competitors appear to have made even heavier gains. The following table gives the Steel Corporation's per cent. output of pig iron, steel ingots and steel rails in 1901, 1908 and 1910, compared with the country's total percentage output of similar products:

	1910	1908	1901
<i>Pig Iron:</i>	Per cent.	Per cent.	Per cent.
Produced by U. S. Steel.....	43.2	43.5	43.2
Produced by other manufacturers....	56.8	56.5	56.8
	100.0	100.0	100.0
	1910	1908	1901
<i>Steel Ingots:</i>	Per cent.	Per cent.	Per cent.
Produced by U. S. Steel.....	56.0	56.4	66.2
Produced by other manufacturers....	44*	43.6	33.8
	100.0	100.0	100.0

*Estimated.

	1910	1909	1902
<i>Steel Rails:</i>	Per cent.	Per cent.	Per cent.
Produced by U. S. Steel.....	57.9	54.7	64.8
Produced by other manufacturers.	42.1	45.3	35.2
	100.0	100.0	100.0

On Feb. 24th the potash factory of A. Mendelsohn's Son in Albany, N. Y., was destroyed by fire, entailing a loss of over \$100,000.

The German trade journals report a German patent for the production of a rubber substitute from the Soya bean oil, by means of nitric acid. It is claimed that the product, after washing with alkali, can be vulcanized in the same manner as rubber.

On March 9th the entire works of the Lafin-Rand Powder Co. at Pleasant Prairie, Wis., 50 miles north of Chicago, were destroyed by a terrific explosion.

Fire destroyed the canning and packing plant of the Pratt Oil Works in Williamsburg on March 11th and also burned out a pier loaded with cans awaiting shipment. A Standard Oil tug moored close by was also destroyed.

Platinum has been advancing in price very rapidly in the last few weeks. Hard platinum (containing 10 to 20 per cent. iridium) has risen to \$43 per ounce and ordinary platinum to \$41 per ounce. The highest previous price was in Dec., 1906, when hard platinum sold for \$40 and the soft for \$38. The lowest price in recent years was in 1905 at \$18.50 per ounce.

Iron Age reports an interesting case of corroded steel framing over a boiler plant in the basement of a building discovered just in time to prevent the collapse of a floor. The corrosion of metal by cinder concrete is not uncommon, but a case like this in question is very rare. The boilers rose within a few inches of the bottom of the I-beams of the floor above them. This floor was formed by terra cotta blocks sprung between the I-beams and covered with concrete and tile. The ventilation in the boiler room was very poor, and ashes were raked from the furnaces and wet down in front of the boilers; the steam rose against the ceiling and passed up through the openings which had been cut in the floor to allow steam pipes to rise. The steam from the ashes unquestionably carried acid fumes, and it must have been more or less condensed on reaching the level of the cool tile, which is so porous that more or less of the damp air undoubtedly penetrated into the fireproofing. The steel about the bay through which the steam pipes rose was found to be so badly corroded that the web of a channel beam was completely gone at one place, tie rods were injured so as to be useless, and the upper flanges of steel beams were practically destroyed. In every case the corrosion was apparently due to acid moisture. No defects were found in the beams in

other bays, although examinations were made. Possibly the most astonishing condition discovered was the fact that a column composed of channels connected by plates was completely full of water. This was discovered when a hole was drilled into the column to ascertain if the material had been injured in any way.

Graphite for lubricating purposes is continuing to increase in use. The Joseph Dickson Crucible Co. reports that in 1910 they supplied 210 steam railroads and 91 automobile manufacturers. This represents an increase with steam railroads of 53 per cent., and with automobile manufacturers of 260 per cent. over the preceding year.

Agricultural experiment stations report two more plants have been found to possess value and commercial possibilities. One of these is the Lechiguilla of southwestern Texas, the fibre of which is in demand for ropes, twine and bagging. The other is the Candelilla, which grows in the Rio Grande region, from which one of the best vegetable waxes—candelilla wax—is obtained. The manufacture of candelilla wax was begun about a year ago in the States of Coahuila and Nueva Leon, Mexico, and a large factory is now in the course of construction on the Rio Grande, south of Sierra Blanco, Texas. It is stated that land which is "unfit for other purposes can now be made to yield an annual revenue from the candelilla of \$100 to \$150 an acre.

The Kansas Legislature has passed a bill which is now awaiting the signature of the Governor, regulating the sale of concentrated cattle foodstuff, forbidding its adulteration and providing for its inspection and analysis.

The Calumet and Hecla Mining Company, with the dividend payable March 25th, will have disbursed, on account of dividends since the organization of the Company, \$114,850,000.

Professor C. E. Munroe, of Washington, was appointed to investigate and report upon the matter of a reduction in the price of gas and electricity for the City of Baltimore. He recommends that the Consolidated Gas, Electric Light and Power Company should be required to manufacture gas by the Cook Oven Method, or by another method which would be equally efficient, as it would then be possible to sell gas at a lower price; he also advises that the London Sliding Scale be adopted with proper modifications to meet local conditions, and that concessions be made in the candle power requirements, provided the price of gas be reduced to 80 cents per thousand feet.

N. H. Darton, for many years connected with the U. S. Geological Survey, has been appointed geologist of the U. S. Bureau of Mines with headquarters at

Washington. He will continue his investigations of the geological conditions under which explosive gases occur in coal beds.

On Feb. 10, 1911, Leo Eliel, a vice-president of the American Pharmaceutical Association, and one of the most prominent men in pharmacy in this country for upwards of fifty years, died suddenly at the age of 66 years. Mr. Eliel was also a member of the U. S. Pharmacopeial Revision Committee.

On March 2nd Prof. Jacobus Henricus van't Hoff, of the University of Berlin, the famous Dutch chemist and a Nobel prize winner in 1901, died in Berlin. He was born in Rotterdam in 1852, and studied at the Universities of Leyden, Bonn, Paris and Utrecht. He became a teacher in 1876 at the veterinary school at Utrecht, in 1878 was called to the University of Amsterdam and in 1896 went to Berlin.

Among his more important writings are: Chemistry in Space (1875); Observations on Organic Chemistry (1881); Studies in Dynamic Chemistry (1884); Laws of Chemical Dynamics (1885); Theoretical and Physical Chemistry (1898-1900); The Salinity of the Ocean (1905). He was editor of the *Zeitschrift für Physikalische Chemie*.

Dr. William Barker Hills, associate professor of chemistry at Harvard University from 1889 to 1904, has been appointed emeritus associate professor.

By the death of Dr. Christian A. Herter a vacancy was caused in the "Board of Consulting Scientific Experts" to the Secretary of Agriculture, which has been filled by the appointment of Prof. Theobald Smith, of Harvard University.

The Helmholtz Medal of the Berlin Academy of Sciences was awarded to Prof. van't Hoff a short time before his death.

The Frederick Sheldon traveling fellowship of Harvard University has been awarded to Latham Clarke, Ph.D., instructor in industrial chemistry.

At the March meeting of Trustees of Columbia University they announced the donation of a new building for the Avery Library and School of Architecture. This is a much needed addition for the University equipment, and ground was at once broken and the work is now under way. It is particularly interesting to the chemists because the space on the top floor of the present building of chemistry, now occupied by the Department of Architecture, will be made available for the extension of the Havemeyer Laboratories which are very much overcrowded. It is planned to have the building for architecture completed by the Fall of 1912, and the new laboratory equipment for chemistry installed in its place by that time.

The sum of \$25,000 required for the purchase of the site for the new chemical laboratories of University College, London, has been completed by a gift of £4,500 from Mr. Ralph C. Forster. The total sum required for the purchase of the site and the erection of the laboratories was £70,000.

The University of Illinois is requesting from the legislature this year for maintenance and general equipment \$2,201,000; for new buildings, \$1,150,000; for maintenance of the College of Medicine, \$200,000; for the College of Agriculture, \$1,575,750. In addition to the above the mining interests of the State are supporting a bill for an appropriation of \$240,000 for the construction of the mining engineering building and maintenance of the department of mining engineering. The ceramic interests are supporting a bill for an appropriation of \$45,000 for the department of ceramics.

Dr. Th. Paul, professor of chemistry at Munich, has been appointed director of the laboratory of inorganic chemistry at Leipzig, to succeed Professor Ernst Beckmann.

Alexander Smith, professor of chemistry at Chicago University, has been appointed Mitchell Professor of Chemistry in Columbia University. Professor Smith is a native of Scotland, a graduate of the University of Edinburgh, and took his doctor's degree at Munich; since then he has taught chemistry at the University of Edinburgh, Wabash College, and the University of Chicago. He will take charge of the Division of General Inorganic Chemistry in Columbia in July.

Editor of Journal of Industrial and Engineering Chemistry:

The editorial in the January number of the JOURNAL entitled "Antiquated Customs" is interesting, and much to the point, and I concur heartily in the statement that the so-called "English," "Newcastle" or "Liverpool" alkali tests are irrational, unscientific, venerable and hoary.

I must take issue, however, with the statement that manufacturers look upon these tests in the light of "gospel revelation." We have never, in the history of our Company, used other than the exact method of calculating the percentage of the Na_2O present, based on the atomic weights of the elements which gives our sodium carbonate the equivalent of 58.49 per cent. Na_2O .

W. D. MOUNT,
MATHIESON ALKALI WORKS,
SALTVILLE, VA.

Editor of Journal of Industrial and Engineering Chemistry:

The following error is noted in my paper on "The Determination of Arsenic and Antimony in Copper," Vol. 3, 1911, page 79, first column, paragraph 5, which should read: "When the sample contains less than 0.0100 per cent. of arsenic plus antimony," instead of 0.1000 per cent. as originally printed.

Also add to paragraph 7, second column, page 79, "Hydroxylamine can be used to better advantage than SO_2 gas, in dilute HCl, (1 : 2) for preliminary separation of Se plus Te from arsenic, etc."

GEORGE L. HEATH.

CONSULAR AND TRADE NOTES AND ABSTRACTS.

SILK INDUSTRY IN JAPAN.

Consul David F. Wilbur reports that the total export of silk of all kinds from Japan in 1910 amounted to \$66,229,794, nearly all of which was exported from Yokohama. The silk produced in Kyoto is of better quality than that exported and is used almost entirely by the Japanese.

The following is the latest report by the Government on the scale of wages paid and the number of employees in the cultivation and manufacture of silk:

	Men.		Women.		Children under 14.	
	Number.	Wages.	Number.	Wages.	Number.	Wages.
Employments.						
Silk culture..	7,028	\$0.20	132,360	\$0.12 $\frac{1}{2}$	11,238	\$0.06
Spinning....	15,059	0.35	65,126	0.25	5,845	0.11
Weaving....	9,983	0.35	63,057	0.25	11,275	0.12
Dyeing.....	3,784	0.60	1,609	0.35	346	0.12
Total.....	35,824	262,152	28,704

All workpeople take holidays on the 1st and 15th of each month and on national holidays.

FRENCH WINE PRODUCTION AND PRICES.

According to a statement just issued by the Bureau of Indirect Taxes, the 1910 wine crop of France, not including Algeria and Corsica, amounted to 753,676,459 gallons, with stocks on

hand of 92,368,865 gallons. These figures are the smallest recorded since 1890. Corsica also fell below the average, with a production estimated at 3,778,556 gallons. Algeria, on the other hand, was favored with a comparatively large crop, amounting to 222,263,887 gallons. The following table summarizes the production in France during the last five years:

Years.	Production. Gallons.	Value.	Area cultivated. Acres.	Average yield per acre. Gallons.
1906.....	1,375,774,273	\$184,562,808	4,195,498	328
1907.....	1,745,381,311	215,647,320	4,075,134	428
1908.....	1,599,424,295	186,317,550	4,088,006	393
1909.....	1,438,296,493	192,936,689	4,016,996	358
1910.....	753,676,459	214,250,047	3,997,302	188

WORLD'S PRODUCTION OF TOBACCO.

The following statistics are compiled from a recent article in the *London Economist*: The total production of tobacco for the year 1909 is given as 1,861,414,648 pounds, while the consumption for the fiscal year was 1,883,399,548 pounds. The discrepancy is charged to the contradictory returns in the United States, which produces by far the largest quantity of tobacco, its production in 1909 amounting to 949,357,000 pounds, as against 718,061,000 pounds in 1908.

The other important tobacco-producing countries are:

Russia.....	207,417,000 pounds
Hungary.....	143,477,000 pounds
Japan.....	91,327,000 pounds
Ottoman Empire.....	76,555,000 pounds
Germany.....	62,104,000 pounds
France.....	50,977,000 pounds

WORLD'S CONSUMPTION OF TOBACCO.

The following statement shows the consumption of tobacco per head of the population, and the amount of taxation per inhabitant, the countries being arranged according to the amount of tobacco used per head:

Countries.	Consumption per capita. Pounds.	Taxation per capita.
Netherlands.....	7.5	\$0.015
Belgium.....	6.2	0.216
United States.....	5.7	0.907
Cuba.....	5.1
Switzerland.....	4.7	0.149
Denmark.....	4.6	0.174
Argentina.....	4.0	1.559
Germany.....	3.5	0.372
Sweden.....	3.4	0.268
Austria.....	3.0	1.181
United Kingdom.....	2.0	1.688

It will be seen that where the taxation presses most lightly the consumption per capita is highest. In England the amount of taxation per capita, \$1.688, is second only to New Zealand, which has the extraordinary total of \$2.68 and France with \$1.91.

CHILEAN TRADE AND INDUSTRIAL NOTES.

During 1910 stock companies were incorporated with an aggregate capital of \$3,597,730, United States gold. The exports from Chile for the first ten months of 1910 amounted to \$82,878,545, against \$80,247,390 for 1909.

The vineyards of Chile cover 157,286 acres, with 257,000,000 vines and a production of 56,234,400 gallons of wine.

The Chilean Government has just placed contract for 140,000 tons of domestic coal for use on the Government railroads, at from \$5.38 to \$6.11 per ton, according to quality.

The Chilean custom receipts for January, 1911, amounted to \$3,872,209, United States gold, against \$3,024,782 for the same period in 1910, of which imports supply about 45 per cent. of the increase.

CHINESE WAGES AND COST OF LIVING.

Vice Consul-General W. R. Dorsey reports the following statistics of wages, price of foodstuffs, etc., for his consular district, which embraces about 50,000 square miles of territory and at least 20,000,000 inhabitants.

Wage rates in United States currency are:

Machinists.....	40 to 75 cents per day
Blacksmiths.....	38 cents per day
Carpenters.....	25 cents per day
Electricians.....	40 cents per day
Stonemasons.....	15 cents per day
Bricklayers.....	15 cents per day
Molders.....	60 cents per day
Plasterers.....	20 cents per day
Stonecutters.....	25 cents per day
Farm laborers.....	30 cents per day
Common laborers.....	20 cents per day

The cost of foodstuffs and clothing such as the natives use are as follows:

Fresh pork.....	15 cents per pound
Salt pork.....	10 cents per pound
Sausage.....	07 cents per pound
Ham.....	20 cents per pound
Flour (foreign).....	03½ cents per pound
Flour (native).....	02½ cents per pound
Sugar.....	04 cents per pound
Tea.....	15 cents per pound
Rice.....	03 cents per pound
Muslins.....	06 cents per yard
Calico.....	07½ cents per yard
Woolens.....	25 cents per yard
Shoes.....	40 cents per pair

QUOTATIONS OF GERMAN INDUSTRIALS.

Wechsler, of Berlin, and Falk, of Dusseldorf, have just published a set of tables showing the course of the principal stock exchange values in Germany for the last ten years. The table for 1909 and 1910 follows:

Shares.	Average dividend 1909-10. Per cent.	Average price 1909.	Average price 1910.
Coal and iron.....	7.87	187.96	195.73
Cement.....	9.22	179.34	168.55
Land companies.....	5.75	152.65	147.80
Textiles.....	7.85	159.99	166.12
Electrical.....	8.25	150.77	162.58
Shipping.....	5.25	121.63	129.08
Chemical.....	15.05	265.20	288.93

EGYPT'S RECORD-BREAKING COTTON CROP.

Consul D. R. Birch advises that the 1910 crop will break the record for Egyptian cotton production. It is now the opinion even among the more conservative merchants that the crop will exceed 725,000,000 pounds. There is this season a higher proportion of better qualities and altogether the crop of 1910 is the most valuable ever grown in Egypt.

BRITISH PROGRESS IN ARTIFICIAL SILK MAKING.

Consul Augustus E. Ingram, Bradford, reports that the use of artificial silk is becoming more and more popular in Bradford. Light cotton voile goods, figured in artificial silk, are now being produced in fair quantities. Cloths composed entirely of artificial silk are rarely, if ever seen, most of the fabric being composed of cotton warp and a weft of artificial silk.

One manufacturing firm of North Wales uses the cuprammonium process and makes an artificial thread consisting of pure cellulose from cotton, and a large portion of the fabrics so made are for the United States.

It is claimed that these artificial silk yarns are now able to resist the severe treatment which fabrics have to undergo in the processes of bleaching, dyeing, and finishing.

At Great Yarmouth an artificial silk plant has been erected to ultimately have a capacity of 13,200 pounds of artificial silk per week.

ARGENTINA'S GLAZED KID PRODUCTION.

Consul-General R. M. Bartleman, of Buenos Aires, reports that the glazed kid shipments from the United States enormously increased last year, when the total value was \$16,675,613, against \$4,747,063 in 1909, and only \$2,930,179 worth in 1908.

GAS IN LATIN AMERICAN CITIES.

Consul-General Bartleman reports that gas in Buenos Aires costs 8 cents per cubic meter (about \$2.40 American gold per

1,000 cubic feet) for lighting, and one-half that price for power purposes.

Vice Consul-General Guyant writes that the new gas works at Mexico City charges 5 cents gold per cubic meter, with a discount of 10 per cent. to the average consumer and further discounts to large consumers until the lowest net rate reaches 3 cents per cubic meter (about 90 cents per 1,000 cubic feet).

Consul-General Deitrich states that the gas company at Guayaquil, Ecuador, charges 20 cents silver per cubic meter (about \$3 American gold per 1,000 cubic feet), plus 40 cents silver (about 20 cents gold) for rental of meter, the internal revenue stamps required to be affixed to all bills, receipts, etc.

BRAZILIAN CONCESSION FOR STEEL PLANT.

On February 25, President Fonseca signed a decree granting two Brazilian capitalists a 25-year concession for a 150,000-ton steel plant in the State of Minas Geraes, with a subvention of \$3 a ton on ingots, \$8 a ton on rails, plates, and structural material, and \$10 a ton on certain other material.

The Government is pledged to take 50,000 tons annually, and it is restricted from buying foreign-made material, unless the inspectors prove that the material made at the new plant is inferior. The concessionaires are exempted from duty on coal and coke and will receive preferential rates on the Government railroads.

PETROLEUM.

Production of oil in the Baku district in Russia in 1910 is reported at 478,500,000 poods, or 7,834,480 metric tons; a decrease of 11,800,000 poods, or 2.2 per cent. from the previous year.

The production of crude petroleum in Roumania in 1910 was 1,357,000 metric tons, an increase of 60,000 tons, or 4.6 per cent. over the previous year.

CANDY.

The exports of confectionery from the United States during the year ended June 30, 1910, amounted to \$784,692, of which \$305,998 worth went to the United Kingdom, \$118,961 to Canada, \$48,944 to Cuba, \$39,245 to Australia, \$37,677 to Panama, \$35,245 to the Philippines, and \$198,622 to all other countries.

CHINESE TRADE AND INDUSTRIAL NOTES.

Consul-General Bergholz, of Canton, reports that a factory equipped with British machinery for degumming and manufacturing ramie fiber has been completed at Kow Kong.

Consul-General Anderson reports that shipments of tin from China are likely to be soon largely increased. German interests have secured concessions in the Province of Yunnan, and are installing modern ore dressing and smelting machinery. The average production of these mines for the past five years has been approximately two and one-half million dollars. The great proportion of this tin is shipped to the United States. It is expected that the new methods and modern plants will materially increase this production.

Official reports place the number of Para rubber trees cultivated in Cochine, China, at over 1,000,000, of which 15,000 are now being tapped. 4,000,000 additional trees will be planted this season.

There is a constantly growing demand among the Chinese for soaps of foreign manufacture. The total imports of soap into the Empire amounts to nearly a million dollars a year. Of the imports of 1908 about one-half came from Great Britain;

one-sixth from Japan; 13 per cent. from Austria-Hungary; and about 12 per cent. from Hong Kong. The United States furnished about four-tenths of 1 per cent.

EXPORTS OF RUBBER FROM BRAZIL.

Consul George H. Pickerell, Para, reports the following exports of crude rubber from the Amazon River district (from Para, Manaus, Iquitos, and Itacoatiara) during the calendar year 1910, as compared with the exports of 1909:

To United States.			
Total in 1910.		Total in 1909.	
Metric tons.		Metric tons.	
7,303.8	Fine	9,493.6	
1,363.7	Medium	1,790.9	
4,319.7	Coarse	5,878.3	
1,627.1	Caucho	2,678.6	
14,614.3		19,841.4	

To Europe			
Total in 1910.		Total in 1909.	
Metric tons.		Metric tons.	
11,656.7	Fine	9,817.4	
1,811.3	Medium	1,927.0	
3,364.6	Coarse	2,968.9	
6,149.6	Caucho	5,116.3	
22,982.2		19,928.6	

HEAVY IMPORTS OF PLATINUM.

The consumption of platinum in the United States increased considerably in 1909 over that of the preceding year. The domestic production decreased somewhat, but the imports, from which practically the entire supply is obtained, more than doubled.

According to an advance chapter from "Mineral Resources of the United States, Calendar Year 1909," on the production of platinum and allied metals, prepared by Waldemar Lindgren for the United States Geological Survey, the value of the platinum imports in 1909 was \$2,973,948, as against \$1,229,873 in 1908. The figures for 1909 are the highest on record except those for 1906. The advance chapter, in pamphlet form, may be obtained free by applying to the Director of the Survey at Washington.

The production of platinum in this country is small, for all that is obtained comes as a by-product in working the gold placers of California and Oregon.

During 1909 the use of platinum in the jeweler's trade increased considerably, gaining favor as a mounting for precious stones and as a material for watch chains and necklaces.

The report gives statistics of foreign and domestic production for several years, and considers also the use and the supply of iridium, osmium, and palladium, rare metals allied to platinum. None of these metals was produced commercially in the United States.

Iridium is used principally for hardening platinum alloys. In 1909 the imports of iridium amounted to 341 pounds, valued at \$135,878, the average cost being about \$33 per troy ounce. The cost is rapidly advancing and was quoted at \$60 per troy ounce in October, 1910.

Osmium is used to a small extent in some kinds of incandescent lamps. It is quoted at \$33.70 per troy ounce. Palladium, which is well adapted for parts of astronomical instruments and certain dental work, sells at \$34 per ounce, and pure rhodium, which is of considerable value in making high temperature determinations, is quoted at \$155 per ounce.

PRODUCTION OF FULLER'S EARTH.

The production of fuller's earth in 1909 is just reported in an advance chapter of the Geological Survey's volume "Mineral Resources of the United States, Calendar Year 1909."

More than half the fuller's earth produced in the United States is mined in Florida, but the entire domestic production supplies only three-fourths of the home demand, about one-fourth of the amount used being imported. The value of the total production in 1909 was \$301,604; the imports were valued at \$101,151.

Fuller's earth has been largely used for cleaning grease from cloth and furs, but it is now chiefly used in this country for clarifying oils. The report discusses the chemical composition of the material and presents theories to account for its peculiar properties.

GREAT POSSIBILITIES OF POWER DEVELOPMENT IN ST. LAWRENCE RIVER BASIN.

Possibilities of water-power development along the streams making up the St. Lawrence River drainage system received special consideration in a report on the surface water supply of the basin prepared by C. C. Covert, A. H. Horton, and R. H. Bolster for the United States Geological Survey and published by the Survey as Water-Supply Paper 264. Copies of this paper are now available for free distribution and may be obtained on application to the Director of the Survey at Washington, D. C.

The Survey's report gives figures showing the flow of the rivers in the basin and notes the conspicuous features of each stream. The statistics have been gathered by daily observations extending over at least a year.

JUAN OIL FIELD, UTAH.

Nearly 10,000 claims have been filed for locations in the San Juan oil field, Utah, during the last few years. Development has not, however, kept pace with the filing of the claims, for although a great deal of drilling has been done most of it has been unskilful, and strings of tools have been lost in many of the drill holes sunk. As a result, although 25 wells have been drilled, none are yet producing commercially.

Oil was encountered, however, in nearly every place where drilling was attempted, and in the opinion of H. E. Gregory, of the United States Geological Survey, whose report on the

field is published as a part of the Survey's Bulletin 431-A, now available for distribution, several of the wells already sunk are likely to prove profitable.

APPROPRIATIONS FOR THE WORK OF THE UNITED STATES GEOLOGICAL SURVEY.

Most of the appropriations for the work of the United States Geological Survey are included in the great Government supply bill known as "An act making appropriations for sundry civil expenses of the Government," popularly called the "sundry civil bill." The bill for the fiscal year closing June 30, 1912, contains appropriations for Survey work amounting to \$1,205,520. The principal items are as follows:

Topographic surveys.....	\$350,000
Geologic surveys.....	300,000
Mineral resources of the United States.....	75,000
Chemical and physical researches.....	40,000
Geological maps of the United States.....	110,000
Gaging streams, etc.....	150,000
Surveying national forests.....	75,000

The bill also appropriates \$165,000 for printing and binding Survey reports, to be expended by the Public Printer.

In addition to these amounts the sum of \$100,000 for surveys in Alaska was included in the urgent deficiency act, approved December 23, 1910, and the sum of \$37,400 for rents was appropriated in the "legislative bill," making a grand total of about one and a half million dollars.

SAND LIME BRICK.

The United States Geological Survey has just published a report by Jefferson Middleton on the production of sand-lime brick in 1909, an advance chapter from the Survey's volume "Mineral Resources of the United States, Calendar Year 1909." The pamphlet can be obtained free by applying to the Director of the Survey at Washington, D. C.

MINERAL LAND NOW WITHDRAWN FROM ENTRY.

The areas of public mineral lands of all kinds now withdrawn from public entry are given below in acres:

Coal.....	80,007,688
Oil and gas.....	3,796,572
Water power.....	1,403,054
Phosphate.....	2,548,145

BOOK REVIEWS.

Cane Sugar: A Text Book on the Agriculture of the Sugar Cane, the Manufacture of Cane Sugar, and the Analysis of Sugar House Products together with a chapter on the Fermentation of Molasses. By NOEL DEERR, Sugar Technologist at the Experiment Station of the Hawaiian Sugar Planters' Association: Author of "Sugar and the Sugar Cane." xvi+592 pp. Royal 8vo., 280 illustrations. Norman Rodger, Altrincham (Manchester). 1911. 20s. net.

This admirable treatise upon the cultivation of sugar cane and the manufacture of sugar therefrom is a substantial enlargement upon a former edition, published in 1905. The new edition contains 592 pages as against 396 in the first edition and as the new pages contain more than the old, on account of their increased size, the contents are more than proportionally greater than the mere numbers of pages would indicate.

The author, in thus amplifying his former work, has introduced much material drawn from his own wide experience, thereby adding directly to the store of knowledge of this particular subject. Very evident is his desire to bring the matters treated of into the range of practicability and to indicate clearly, by a historic method of discussion, the trend of modern advances so as to assist the reader to judge of the most advantageous methods.

Various topics are mathematically discussed to good advantage, as the setting of mills, etc., the maceration of cane during crushing, many problems of evaporation, etc. The work is abundantly illustrated with good cuts, photographs and excellent colored plates. It would be an advantage to have the colored plates of the different varieties of sugar

cane all made life-size or of a uniform proportional size instead of being drawn to scales variously represented at $\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{4}$, and full natural size.

The early chapters deal, in considerable detail, with the varieties, natural and artificially derived, of the cane and its requirements of climate soil and moisture. The discussion of soils emphasizes the confusion arising from analyses made by attacking soils with reagents varying from weak citric to strong hydrochloric acid to effect the initial solution.

A practical summary of fertilizer requirements is given with concise formulae, and directions for typical cases and the important functions of lime are not overlooked, while an interesting discussion of the lime-magnesia ratio for sugar cane soils is included. Irrigation is shown to have influenced so profoundly the yield of cane in many localities that it certainly is a strong argument for this system where water is to be had, especially in view of the possible economy of pumping as exemplified in the Hawaiian Islands where the cost has been reduced to ten cents per million gallons for each foot of elevation. Entomologists will find an interesting chapter on insect pests and various means of combatting them and their ravages.

In the harvesting of cane, the author, like many others, evidently looks hopefully forward to a satisfactory mechanical cane cutter to replace the present expensive though efficient manual labor. All varieties of transportation, loading and unloading are well treated and illustrated.

In an extended chapter on milling cane, he advocates the 12-roller mill as permitting double maceration. Twenty or twenty-five per cent. of water, thus added, is shown to give the best results, with an extraction of 95 per cent. of the total sugar. Diffusion cannot improve on this without the expenditure of much extra fuel. In no case is there reason to suppose that increasing the extraction will decrease the amount of available sugar due to a lower purity. In defecation he seems to favor the Deming system, though without superheating. The carbonation process is carefully described and said to be used in only a few places beside Java, and authors are quoted as claiming that it destroys sucrose as well as glucose. The fact is it can be so conducted as to destroy no sucrose and but little glucose.

The author advocates filtering juice when making sugars for direct consumption.

In the chapter on multiple evaporation, every phase of the matter receives thorough concise discussion. The Kestner is spoken well of for preheating. Central condensers are recommended for pans and multiple effects on account of the economy of management. Some advanced constructors, however, prefer individual condensers, as affording more perfect control of boiling.

The theory of crystallization is interestingly dealt with and practical features of boiling and of centrifuging sugars are well described. The theories pertaining to formation of molasses occupy the following chapter. A full discussion of megass furnaces and

the problems relating to megass as fuel are given. One is warned against the error of attaching too much weight to the fuel value of sucrose in megass. The author speaks hopefully of paper-making from megass.

The next section of the book takes up analytical methods and opens with a good chapter on polariscopes, including Bates' new model with adjustable sensitiveness. In describing the various methods of clarification of sugar solutions for analysis he endorses Horne's method of defecation with anhydrous subacetate of lead. Other chapters treat of sugar house methods of analysis and factory control, including the needed practical directions. Fermentation and the distillation of rum and alcohol receive attention next, including a tentative method of distillery control, and analytical methods. He finds 90 per cent. of the theoretical alcohol can be obtained from the combined sugar and glucose in molasses.

These chapters are followed by an appendix, numerous useful tables and an index.

Not one per cent. of the many interesting and valuable features of this work can be even briefly referred to in this short notice. The book is replete with essential information, is agreeably written, suggests a multitude of attractive themes and, in short, is such that no sugar man can afford to be without.

W. D. HORNE.

Testing Milk and Its Products. A Manual for Dairy Students, Creamery and Cheese Factory Operators, Food Chemists and Dairy Farmers. By E. H. FARRINGTON and F. W. WOLL. Twentieth Revised and Enlarged Edition. 297 pages. Madison, Wis. Mendota Book Co. 1911.

This well known manual now appears in its 20th edition, revised and brought to date. The authors have succeeded in presenting a book which can be followed by those of little scientific training in the control of dairy products. While the work is, in the main, a textbook, it is remarkably free from a didactic style. The subject matter is clear and concise and is further aided by illustrations and examples.

Because of the almost universal application of the Babcock test, a detailed account of this method is given. Errors arising from different causes are pointed out and the procedure for obtaining the most favorable conditions is fully described.

A noticeable feature of the book is the attention given to the operation of the dairy. The various factors influencing the yield and quality of milk, methods for collecting and testing at the dairy, the butter and cheese yield and the calculation of dividends from the amount of butter fat delivered by the various patrons are discussed. For those who have the ability and equipment, the usual quantitative tests made on milk and its products are given.

An appendix gives the various government, state and city standards together with useful tables applicable to dairy operations.

To assist in an understanding of the text a list of questions is given at the close of each chapter.

Suggestions are also made relative to the organization of co-operative creameries, and cheese factories.

The practical nature of the book, together with its

simple and comprehensive treatment, should commend itself to the various dairy interests. A. GROSS.

Electricity Experimentally and Practically Applied. By SIDNEY WHITMORE ASHE. 349 pages, illustrated. D. Van Nostrand Co. \$2.

A textbook for the beginner and the practical man. The discussion of the principles of electricity, its exposition of experimental work, and its application of laboratory results to the problems and operations of the business world is clear and easy to follow. The aim has been to make the explanations as simple as possible and to keep the practical features that engage attention. The author has been teaching electrical engineering to the employees of corporations, such as the Brooklyn Rapid Transit Company, the Edison Illuminating Companies of New York and other cities, and is now directing specialized educational work for the General Electric Company at Harrison, N. J., and through this experience has acquired an unusual understanding of the limitations and needs of working electricians and has developed a capability for the presentation of the subject to such students. The book is adapted primarily to the requirements of practical electricians who desire to increase their knowledge of electricity, and enlarge their capacities for usefulness.

"Metal Statistics for 1911." "Metal Statistics," published by the American Metal Market and Daily Iron and Steel Report. New York. 208 pages. $3\frac{1}{2} \times 6$ inches, bound in cloth.

The 1911 edition of this work contains a larger and better selection of statistical information relating to the metal and iron and steel trades, than any of the previous issues, and the figures are presented in a clear and concise form, and a very convenient and complete reference. It contains all the important statistics covering the production, consumption and price movements of all metal and iron and steel products for a series of years.

The iron and steel section has been entirely revised under the supervision of Mr. B. E. V. Luty, of Pittsburgh, and several new features of original character have been introduced, including "*Composite Pig Iron*," and "*Composite Finished Steel*," which are intended to show, at a glance, the bulk movement of the pig iron and steel products as a whole.

Among the various copper statistics, a table is given showing the total production of this metal for more than one hundred years or from 1800 to 1910 inclusive, which sets forth in a very graphic way the tremendous strides that have been made in this industry within the last ten years.

ABSTRACTS AND NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

A World Trade Directory.

The Bureau of Manufactures, at Washington, under authority of a special act of Congress, is about to publish an international trade directory, containing the names of approximately 125,000 business houses in foreign countries, which are engaged in foreign trade, including every line of industrial, commercial and financial activity. These names have been collected during the past four years by the United States consular officers and special agents. Because of the magnitude of the files, it was possible to distribute the information to the business houses of the United States except through a special publication.

The book will consist of pages $9 \times 11\frac{1}{2}$ inches in size, and is to be bound in buckram. It is to be issued by the public printer through the Superintendent of Documents at a price not to exceed \$5.00 per copy.

As the names in this directory have been classified according to business, country and city, and as the consular officers and agents have made a very thorough canvass of the territories with which they are associated, the directory should be of great use to the business interests of our country.

Florida Phosphate Mining.

The United States Department of Agriculture just published a monograph on the phosphate fields of Florida, by William H. Waggaman, scientist in physical and chemical investigations. The preface to this report contains interesting information regarding the phosphate deposits in the United States, by Frank K. Cameron.

Public attention has repeatedly been directed in the last few years to the phosphate deposits of this country. Grave fears have been expressed that a serious dearth of available phosphates is imminent, and that at a time when their im-

portance, if not necessity, for the agricultural development of the country is coming to be appreciated. These fears are undoubtedly exaggerated, but the agitation has not been without some value. Phosphate deposits of greater or less extent and of varying degrees of richness are being reported from almost all parts of the country, and the most extensive deposit of high-grade rock in the world, lying in the States of Utah, Wyoming and Idaho, is as yet practically untouched. Deposits have been reported in the States of Pennsylvania, New York, North Carolina, Arkansas, Kentucky, Nevada and California, in addition to the well known deposits of Tennessee, South Carolina and Florida. Coincident with the discovery of new deposits in this country there has been considerable activity in the discovery, and especially in the development of foreign deposits notably those of Northern Africa, the South Pacific Islands, France and Belgium.

It is a debatable question whether there is any reason for fearing a world shortage of rock phosphate, but the situation is not without its serious economic aspects for this country. The Florida deposits are worked to an extent far outstripping all other American deposits, and only approached by those of Northern Africa. A large percentage of the best Florida rock is exported to Europe. Indeed, Europe takes only the high-grade rock, and this, together with the fact that Europe takes a larger proportion of high-grade Florida rock than does the United States, has led to alarming reports regarding the control of these deposits by foreign corporations. Foreign corporations are large operators in Florida, but they do not control a major part of the output, and no individual foreign-controlled plant is as large as some of those operated by American capital. A far more serious feature of the present situation is the waste of lower grade rock, incident to the methods of mining. If for economic reasons the best rock must continue to go to foreign markets, it will soon be imperative to devise means of con-

serving and handling what is now wastage for the use of the home consumer.

That the present or any prospective exportation of rock phosphate is likely to impair seriously the resources of this country is very doubtful. The foreign market demands and can handle only the most expensive grades, and other deposits, such as those of the Ocean Islands, Tunis and Algiers, are now supplying more to Europe than are the deposits of Florida. While it may be true that the end of hard rock deposits in Florida is in sight, this is certainly not the case with the pebble deposits, and the vast bulk of other American deposits has been scarcely touched. With the great mass of material in sight of medium and low grade, or unavailable to Europe on account of prohibitive land transportation rates, the great problem is to devise means and methods for making the material as readily available and as cheap as possible to the home consumer. This problem involves the elimination of waste or its reduction in the lowest possible point. At present it appears that this problem must be worked out in connection with the Florida deposits, and the résumé of the conditions now existing, which is given in the bulletin, is not only valuable in itself, but is far more important as a basis for future investigations in the interests of American agriculture.

A general account is given in this monograph of the physical properties and methods of mining the phosphate rock, the location of the deposits, the cost of producing the rock, and the output for the years 1907-9.

Review of the Drug and Chemical Trade 1910.

The 1910 Review of the Drug and Chemical Trade has been issued by the *Oil, Paint and Drug Reporter* under date of February 27, 1911, in the form of a special supplement. This supplement contains 84 pages, covering a comprehensive record of the market development for the year, legislative and judicial happenings effecting them, and an immense mass of statistics showing price changes, production, volume of trade, exports, imports, etc.

This review includes a very comprehensive report of the petroleum industry covering 16 pages of descriptive and statistical matter bearing on the production of petroleum, not only in the United States, but in most of the foreign countries producing commercial quantity. The review is concluded by a statistical report of the imports into the United States of chemicals, drugs, etc., covering a period of five years, ending December, 1910, and shows the number of pounds imported and the value for each year.

This annual review is a valuable summarization of the commercial progress in the drug and chemical trade during the year 1910.

The annual statistical number of the *Engineering and Mining Journal* is laid out upon the same plan as its predecessors, but some new features that are important; among these are the more comprehensive treatment of many of the minor minerals and an exceptionally valuable series of articles reviewing metallurgical progress. Many of the articles are contributed by leaders in the mining and metallurgical industry, and form the basis of an authority and up-to-date review for present conditions obtaining in those industries. Increases are shown in almost all lines of metallurgical production, especially copper, lead, spelter and tin. No material difference is noticeable in the average prices quoted for 1910 compared with 1909. A large number of statistical tables makes this number important for the study of the comparative development in various metallurgical lines for the past year.

The *Journal of the Institute of Metals*, Vol. IV, which is edited by the general secretary, Mr. C. Shaw Scott, contains a series of papers of scientific interests at Glasgow in September.

The papers are as follows:

- "The Heat Treatment of Brass: Experiments on 70:30 Alloy." By Messrs G. D. Bengough and O. F. Hudson.
- "Some Common Defects Occurring in Alloys." By Dr. C. H. Desch.
- "Shrinkage of the Antimony-Lead Alloys, and of the Aluminum Zinc Alloys, during and after Solidification." By Professor T. Turner and Mr. D. Ewen.
- "The Effect of Silver, Bismuth and Aluminum upon the Mechanical Properties of 'Tough Pitch' Copper Containing Arsenic." By Mr. F. Johnson.
- "Metallography as an Aid to the Brass Founder." By Mr. H. S. Primrose.
- "Magnetic Alloys Formed from Non-magnetic Materials." By Mr. A. D. Ross.

The Catalogue of the Second International Rubber and Allied Trade Exhibition, to be held in London, June 24, to July 11, 1911. Executive Offices, 75 Chancery Lane, London, W. C. The Exhibition will include the following general headings:

- Plantation Rubber.
- Crude Plantation Rubber.
- Block, Sheet, Biscuit, Crepe, Worms, Lace, Scrap, etc.
- Wild Rubbers.
- Rubbers from Brazil, Peru, Bolivia, Columbo, Guianas, Mexico, Assam, Borneo.
- Balata, Gutta Percha and Tropical Gums Generally.
- Botanical Specimens.
- Methods of Tapping.
- Tapping Knives.
- Collecting and Coagulating Utensils.
- Machinery of Every Description Required for the Preparation of Rubber (Wild or Plantation).
- Machinery, etc., Required on Rubber Plantations.
- Fertilizers.
- General Rubber Estate Sundries.
- Motor and Other Boats, Motors, and Other Vehicles Used on Rubber Estates.
- Articles not enumerated.
- Manufacturers' Section.
- All goods manufactured wholly or partly of India Rubber, Gutta Percha, Balata, and Asbestos.
- Chemicals, Fillings, etc., used by India Rubber manufacturers.
- Fabrics used in the manufacture of Rubber Goods.
- Machinery, Moulds, Utensils, etc.
- Rubber Substitutes, Reclaimed Rubber, etc.
- Vulcanite and Ebonite.
- Asbestos Goods.
- Articles not enumerated.
- Rubber Literature.

"**Conservation by Sanitation.**" By ELLEN H. RICHARDS. Published by John Wiley & Sons, New York. \$2.50.

Proceedings of American Gas Institute. Fifth Annual Meeting, 1911. 879 pages; bound in cloth.

The Bristol Company of Waterbury, Conn., has just issued a forty-page illustrated catalogue on recording thermometers, including description of the Compensated Gas-filled Recording Thermometer, which was discussed fully in recent issues of engineering and trade papers.

These instruments are being used for a great variety of applications for recording temperatures up to 800 deg. Fahrenheit.

The Work of the Chemist in Conservation. By PROF. ELBERT W. ROCKWOOD. Pop. Sci. Mon., Mar., 1911.

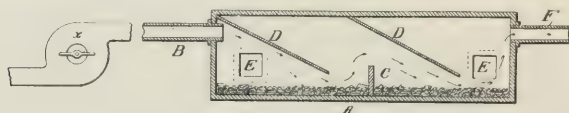
- Preservation of Structural Timbers from Decay. By C. P. WINSLOW. Proc. Eng. Soc. W. Penna., Dec., 1910.
- Sterilization of Water and Disinfection of Sewage. Sterilization of Public Water Supplies. By GEO. A. JOHNSON. J. Assoc. Eng. Soc. Jan., 1911.
- Disinfection of Sewage and Sewage Filter Effluents. By EARLE B. PHELPS. J. Assoc. Eng. Soc. Jan., 1911.
- The Analysis of Paints and Painting Materials. By HENRY H. GARDNER AND JOHN A. SCHAEFFER. New York, 1911. McGraw-Hill Book Co. \$1.50.
- The Elements of the Science of Nutrition. By PROF. GRAHAM LUSK. 2d Edition. Phila., 1911: W. B. Saunders Co. \$3.00.
- The Air We Breathe in Buildings. By Dr. LUTHER H. GULICK. Science. Mar. 3, 1911.
- Handbook of Inorganic Chemistry. By PROF. H. ERDMANN. 5th Edition. Brunswick, 1910: F. Vieweg und Sohn. \$4.00. (German).
- Sewage. By A. PRESCOTT FOLWELL. 6th Edition. New York, 1910: John Wiley & Sons. \$3.00.
- Personal Reminiscences of the Dyestuff Industry. By HERMAN A. METZ. Silk. Feb., 1911.
- Preliminary Announcement, 8th International Congress of Applied Chemistry. By Dr. BERNHARD C. HESSE, 25 Broad St., New York.
- Digitalis Standardization and the Variability of Crude and Medicinal Preparations. By WORTH HALE. Bulletin 74. Hygienic Laboratory Public Health and Marine Hospital Service of the United States. Washington, 1911.
- Scientific and Industrial Bulletin of Rouse-Bertrandtills. Series III, No. 2, Oct., 1910, has appeared and as usual contains much valuable information on essential oils, etc.
- Foods and Their Adulteration. By DR. HARVEY W. WILEY. 2d Edition. Philadelphia, 1911: P. Blakiston's Son & Co. \$4.00.
- Tables for the Determination of Common Rocks. By OLIVER BOWLES. New York, 1910: D. Van Nostrand Co. 50c.
- Ehrlich's Side Chain Theory and the Science of Chemotherapy. By THOMAS J. KEENAN. Amer. Druggist. Feb. 27, 1911.
- Surface Water Supply of the United States, 1909, Part X. The Great Basin. By E. C. LARUE and F. F. HENSHAW. U. S. Geological Survey, Water Supply Paper No. 270. Washington, 1911.
- Descriptive Mineralogy, with Especial Reference to the Occurrence and Uses of Minerals. DR. EDW. H. KRAUS. Ann Arbor, 1911: George Mahr. \$2.75.
- Tomato Ketchup under the Microscope with Practical Suggestions to Insure a Cleanly Product. By B. J. HOWARD. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular No. 68. Washington, 1911.
- Applied Chemistry Abstracts, being Section 6 of the *Journal of the International Institute of Technical Bibliography*. London (57 Chancery Lane), \$6.25 per year, 26 numbers. The name is a misnomer as the publication is a bibliography and does not contain any abstracts.
- Yearly Report on the Advances of Chemistry and Related Division of Other Sciences. By J. TROEGER and E. BAUER. 1905-1908. Brunswick, 1910. \$6.00. (German.)

RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

984,221. Production of Gases of High Oxidizing Efficiency.

The object of this invention is the production of gases of high oxidizing energy, the active properties of which gases result from the contact action of atmospheric air at ordinary temperatures with certain chemicals of such relatively low cost that they may be economically restored to full activity after having become somewhat ineffective, so that the process



may be worked with a minimum of labor and at a very low cost. The gases resulting from this treatment of air may be applied to purposes of combustion, whereby in the use of purely carbonaceous fuel or a mixture of fuel and ore, a very high degree of heat is obtained, and the combustion may be perfected with the relatively smallest volume of air during a stated period; this combined effect results from the highly oxidizing properties of the air, whereby the impurities, such as sulfurous and various organic and inorganic compounds, are rendered unobjectionable. In carrying out the process, atmospheric air is led into contact with a mixture of manganate of soda (or its chemical equivalent manganate of potash), peroxid of manganese, sulphuric acid and chlorid of sodium whereby oxygen, ozone, and chlorine are generated and admixed with the air.

The accompanying illustration shows apparatus in which the process may be advantageously practiced.

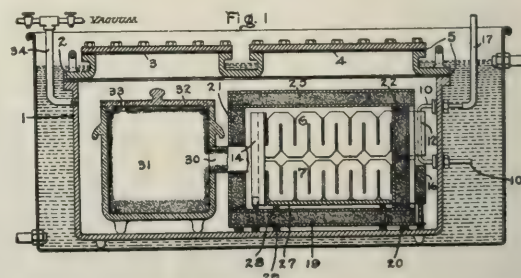
The inventor is Charles Hornbostel, of New York, N. Y.

984,503. Process of Producing Calcium.

This invention relates to the production or recovery of metallic calcium by direct decomposition of calcium carbide in a suit-

able furnace in which the gaseous pressure is materially less than one atmosphere. The electric furnace used for carrying out this operation has an air-tight envelope in which a good vacuum can be produced and maintained and has a hot zone in which the calcium carbide can be heated and decomposed and from which the vaporized calcium can be conducted to a cooling zone for condensation and recovery as substantially pure metal.

Inasmuch as the direct decomposition of calcium carbide into calcium and carbon does not result in the liberation or production of any great quantity of gaseous material, the continuous maintenance of a substantial vacuum in the furnace is easily possible even at the high temperature at which the operation must be carried out. By working in a vacuum, the temperature of decomposition is much reduced and the calcium comes off in pure and unoxidized condition. The operating temperature varies



somewhat with the degree of vacuum and seems to be in the neighborhood of 1500°-2000°, the calcium distilling off at this temperature and leaving behind a pseudomorph of soft unctuous graphite. Alternating current may advantageously be used in the heater grids, and any temperature up to the vaporizing point of carbon can be obtained and constantly

maintained for any length of time at a pressure of a fraction of a millimeter of mercury. The material under treatment does not come in contact with the heating elements and chemical action therebetween is avoided. The main envelope of the furnace is maintained cool by the circulation of water below and on all sides up to a level just below the man-hole covers 3 and 4. These are preferably left unsubmerged for the more ready introduction and removal of the calcium carbide and its decomposition products. In charging and discharging the furnace it is only necessary to remove the covers 3 and 4, whereupon after removal of the upper screen 25, the crucible 26 can be filled with a new charge and the condensing chamber 31 relieved of the condensed material and even lifted bodily out and replaced by another similar earthen pot.

The inventor is William C. Arsem, of Schenectady, New York, and the patent has been assigned to the General Electric Co.

984,645. Process of Producing Large Well-Formed Crystals from Solutions of Different Kinds.

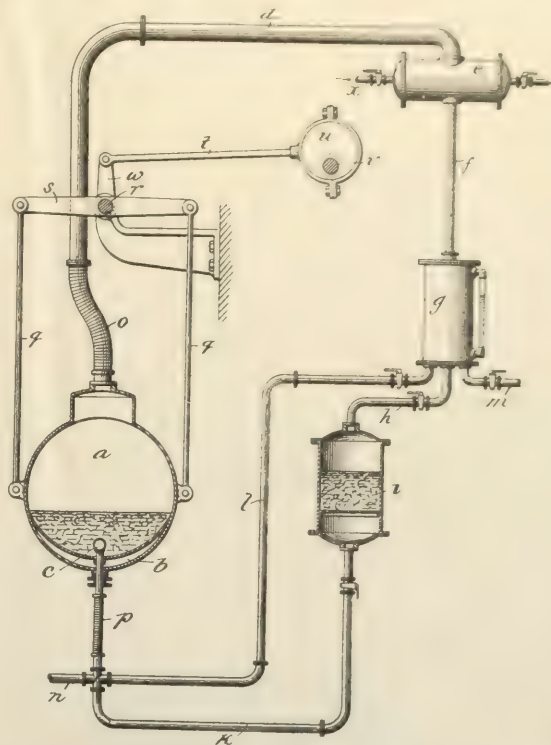
This invention has for its object the growth of well formed individual crystals up to a considerable size, by the evaporation process, in such a way that the crystallizing of the substance is so regulated that in a definite time unit a desired and known quantity of substance crystallizes out, this quantity being alterable as desired, and finally so that the crystallization is regulated to correspond with the taking up capacity of the crystals present, in order, therefore, to reach the optimum of such taking up capacity. The invention also aims to create or influence the crystallization conditions themselves advantageously.

The following examples will illustrate the several modes of procedure in the practice of the process: In a crystallizing apparatus which is connected with a surface condenser and an air pump, 5 kilograms, say, of crystals are introduced, and from 6 to 8 kilograms of concentrated solution are added thereto. The solution is then evaporated by heating the apparatus, the vaporized solvent being condensed in the surface condenser, and the so-formed condensate is then taken up in part in a measuring receptacle, the other part being returned to the apparatus. It has been previously determined, for example, that the quantity of crystals introduced into the apparatus can take up in an hour about 3 per cent. of its weight, *viz.*, 150 grams of the substance. In order to form this quantity hourly on the crystals already present, such a quantity of substance is dissolved in water, *e. g.*, 300 grams of water and this feeding solution are continuously or intermittently introduced into the apparatus during an hour. At the same time, 300 grams of condensate are collected in the measuring receptacle and thus taken out of circulation, while the remaining part of the condensate is returned to the apparatus.

As in an hour, 150 grams of substance and 300 grams of water are fed into the apparatus, while 300 grams of water are led off as condensate, the 150 grams of substance will crystallize on the crystals present.

The process also can be carried through in such a way that by regulating the heating of the apparatus, only 300 grams of condensate are produced, measured and carried off. In this case the heating is regulated by measuring the condensate. The process can also be carried out without the regulation of the heating but with measuring and carrying off of the entire condensate, a like quantity of solvent being led into the apparatus in the feeding solution at the same time. Of course, it is to be understood that a proper crystallization under these conditions takes place only when the quantity of additional substance in the feeding solution corresponds to that which the crystals present are able to take up in the time unit, as any surplus of such substance will form new crystals. In this con-

nection it should be remarked that as certain substances in crystallizing take up water of crystallization, this must be compensated for in feeding in solvent to maintain the concentration of the solution. In some cases, as intimated above, it is necessary to lead back all of the condensate to the apparatus, even when additional feeding substance is not fed



into the latter or is supplied only intermittently. The first or initial crystals which are to be used can be generated in the known manner from the solution itself and will then be left to grow therein, or other crystals, crystal meal or crystal fragments may be introduced into the crystallizing solution.

The ordinary crystallizing apparatus and surface condensers may be used in carrying out the method, the determination of the quantity of condensate being ascertained by an appropriate measuring receptacle or a suitable weighing apparatus, but the accompanying illustration shows a form of apparatus which is particularly well adapted for this purpose.

The inventor is Johanne Bock, of Radebeul, near Dresden, Germany.

984,703. Process of Making Sulfuric Acid and Electrolytic Iron.

This invention relates to the production of electrolytic iron from ferric ores, with the coincident production of sulphuric acid.

According to the invention, a ferric solution obtained by treating a suitable ore of iron with sulphuric acid is first reduced to the ferrous state, and is then subjected to electrolysis with insoluble anodes, the anode being depolarized during the electrolysis by means of dissolved sulphur dioxide.

In practicing the process it is necessary that means should be provided for preventing admixture of the positive electrolyte containing dissolved sulphur dioxide with the electrolyte surrounding the cathodes, for if such admixture should occur, a reduction of sulphur dioxide would take place in the region of the cathode resulting in the contamination of the metallic iron. This reduction of sulphur dioxide is primarily due to the fact that when the acid liquor from the anode compartment is permitted to flow to the region of the cathode there occurs

a considerable evolution of hydrogen by which the sulphur dioxide is quickly reduced.

Moreover, the acid liberated at the anodes or there produced by the oxidation of the sulphur dioxide is distributed throughout the electrolyte, and redissolves the deposited iron at a progressively increasing rate, thereby greatly reducing the efficiency of the operation. By the use of a diaphragm or equivalent means for preventing admixture of the positive and negative electrolytes, the cathode compartment is readily maintained free or substantially freed from sulphur dioxide and sulphuric acid.

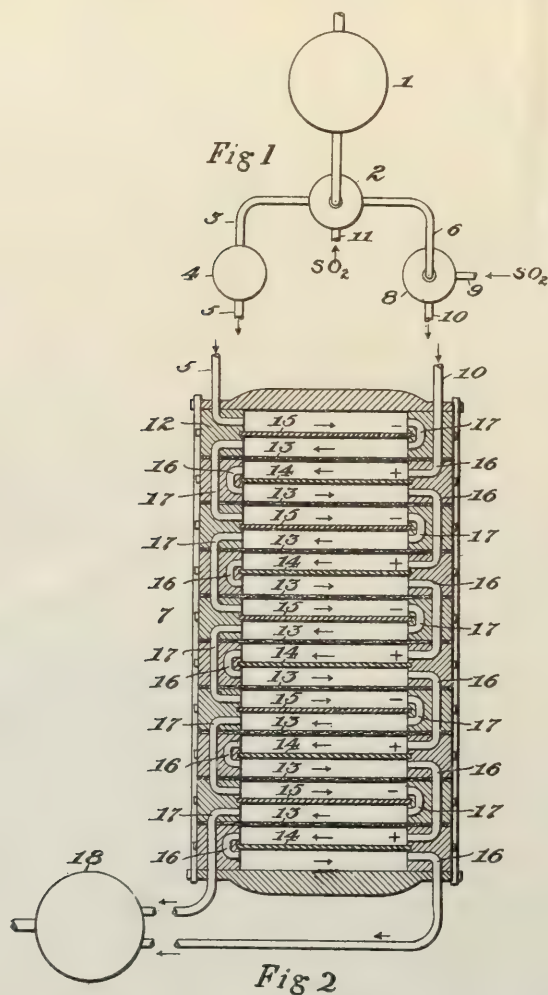
The preferred embodiment of the process is as follows: A ferric ore, as for example, hematite, is dissolved in sulphuric acid, the solution being preferably aided by heat and by the fine division of the ore, with agitation if necessary. The resulting ferric solution is then reduced to the ferrous state, preferably by means of sulphur dioxide, conveniently supplied

is such that the anode and cathode liquors on opposite sides of the several diaphragms flow always in the same direction with respect to each other; that is to say, the flow is relatively uni-directional. This arrangement has been found in practice to be highly effective in avoiding undue diffusion between the several compartments, in cases where porous diaphragms of low resistance and high permeability are employed. Preferably the effluent liquors from both anode and cathode compartments are united in a common receiving tank 18, from which they are removed for utilization.

The inventor is Alexander S. Ramage, of Detroit, Michigan, and the patent has been assigned to the National Tube Company.

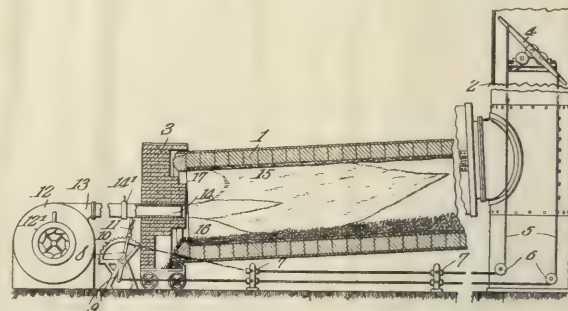
985,313. Burning Portland Cement.

The inventors of this process claim to have discovered that by positively feeding air under superatmospheric pressure to the firing zone of the kiln in sufficient quantities to support complete combustion and to maintain superatmospheric pressure in the firing zone, and by maintaining between the firing zone and the stack a zone of kiln gases under superatmospheric pressure and by utilizing this zone of kiln gases to control the position of the firing zones and by retarding the escape of kiln gases at the stack, thereby increasing the time of contact of the hot kiln gases with the raw materials and causing the operation of the kiln to be independent of atmospheric conditions, the effective intensity of the firing zone is increased and maintained and the cement material reaches the firing zone in proper



in the form of gases from pyrites or sulphur burners. This ferrous solution is then supplied in separate streams to the anode and cathode compartments of a suitable electrolytic cell, that portion of the solution flowing to the positive compartment of the cell, containing an excess of sulphur dioxide and being preferably saturated with the gas. The portion of the electrolyte flowing to the negative compartment is, on the other hand, substantially free from the dissolved gas.

The accompanying illustration shows an electrolytic cell which can be advantageously used in the practice of the process. It will be observed that the arrangement of the several compartments of the cell, and of the intermediate passages,



condition, thereby producing a quick, thorough, incipient fusion of the cement material which results in a clinker that is uniform in size and grade, easily ground and perfectly sound.

In operating a kiln according to this invention, the firing zone usually extends thirty or forty feet into the kiln from the discharge end and is thus under a superatmospheric pressure of from three and one-half inches at the discharge end to three-quarters or one-half of an inch at its inner end. The cushion or zone of kiln gases under superatmospheric pressure will extend usually from the inner end of the firing zone to a point seventy or seventy-five feet from the discharge end of the kiln and its pressure will curve from three-quarters or one-half of an inch at its outer end to atmospheric pressure at its inner end.

The inventors are Fred Leroy Woods and Merlin Boyd, of Iola, Kansas, and the patent has been assigned to the Hunt Engineering Compy.

985,667. Process of Obtaining Sulfur.

This invention relates to the treatment of sulphureted hydrogen and sulphur dioxide for the obtainment of sulphur therefrom, the sulphur being obtained as such, or, if desired, being utilized for the obtainment of sulphur dioxide, sulphuric acid, or sulphuric acid salts. The sulphureted hydrogen and the sulphur dioxide may be in a pure condition, or either of them or both may be mixed with other gases; for example, the sulphureted hydrogen may be contained in coal gas, and the sulphur dioxide in the gases from sulphur burner, in which sulphur is burned with air.

To carry out this invention, the gases containing sulphureted hydrogen and sulphur dioxide respectively are treated, either simultaneously, or one after the other, with a liquid containing, in solution, or suspension, or partly in solution and partly in suspension, such compounds as will cause the sulphureted hydrogen and sulphur dioxide to react upon one another, and sulphur to be obtained. Suitable compounds to assist, or serve as a medium for, this reaction are compounds of metals, the sulphides of which, on the one hand, are insoluble in basic, or in neutral solution and, on the other hand, are decomposed

by mixing in aqueous solution at ordinary temperature a hypochlorite, an ammonium salt and formaldehyde.

PROCESS FOR THE MANUFACTURE OF ANTHRAQUINONE. British Patent No. 16,312/09. Landshoff & Meyer.

Claim: The manufacture of anthraquinone by treating anthracene with a mixture of nitrogen-tetroxide and air with the aid of heat.

PROCESS FOR THE PREPARATION OF TERPENES FROM TURPENTINE OIL. French Patent No. 411,012. Mr. Aladar Skita, Germany.

Claim: A process for the preparation of terpenes from turpentine oil, consisting of heating turpentine saturated with hydrochloric acid with alkaline substances, and a phenol.

PROCESS FOR PREPARATION OF CAMPHENE. French Patent No. 413,282. Terpinwerck, Germany.

Claims: Camphene is produced from pinenhydrochloride which is decomposed by alkali hydroxides and hydroxides of alkaline earths in the presence of substances capable of fixing water.

A NEW DISINFECTANT AND THE METHOD OF PRODUCING THE SAME. British Patent No. 23,230/09. Gebr. Heyl & Co.

Claims: A process for producing a disinfectant and deodorant which consists in digesting cresol which has had its phenol contents reduced, with an acid aluminum sulphate, *e. g.*, a mixture of aluminum sulphate and sulphuric acid and neutralizing the excess acid.

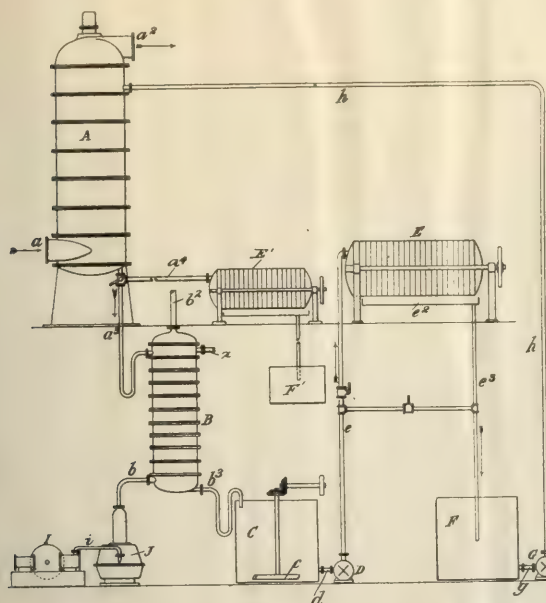
A disinfectant and deodorant produced as described and consisting essentially of a mixture of cresol-sulphuric acid and aluminum sulphate.

METHOD FOR THE PREPARATION OF CONCENTRATED SOLUTIONS OF THIOSINAMINE. British Patent No. 29,247/09. E. Merk, Darmstadt.

Claim: A method for the preparation of concentrated aqueous solutions of thiosinamine, being an improvement in or modification of the method described in Letters Patent No. 22,533 of 1905 and being characterized by the substitution for salicylate of sodium of substances which possess to a certain degree both acid and basic characters, without either the acidic or basic character considerably predominating, such as amido bodies containing acid groups (including glycocoll) or by the substitution for salicylate of sodium of amido esters (including urethane) or salts of alkalies with feeble acids, such as sodium baborate (borax), sodium benzoate, sodium cinnamate, and the like.

MANUFACTURE OF WATERPROOF WASHABLE LINEN. British Patent No. 17,449/09.

Claims: The method of producing waterproof washable linen wherein the linen is treated with starch



by sulphur dioxide alone, or by sulphur dioxide in the presence of air, or other oxidizing agent, or sulphur, or in the presence of a mixture thereof alone or with basic or acid substances.

Such compounds are, for instance, the oxides, hydroxides, carbonates, sulphides, sulphites, thionates, and all basic salts, as well as the acid or neutral weak acid salts of zinc, manganese, iron, or other metals, as well as the neutral or acid salts of these metals with weak acids, the sulphides of which answer the hereinbefore-mentioned requirements.

The manner of carrying out the practice of the process will be explained in connection with the accompanying illustration. In this illustration A is a vertical gas washer and B is an absorption tower, both of these containing a number of superposed chambers. C and F are tanks for liquor. E is a filter-press. D and G are pumps. I is an air compressor and J is a sulphur burner.

It will be presumed that the apparatus is to be used for the extraction of sulphureted hydrogen from coal gas. The gas enters the washer A at *a* and is treated in this washer by the liquor containing zinc thionate. By the action of this liquor the gas is purified and leaves the washer at *a²*.

The inventor is Walther Feld, of Honningen-on-the-Rhine, Germany.

RECENT PROGRESS IN TECHNICAL CHEMISTRY.

MANUFACTURE OF A CHLORAMINE DERIVATIVE. British Patent No. 15,303/09. Charles Frederick Cross.

Claims: As a new product a derivative of the simplest chloramine containing the methylene group.

The manufacture of the new product referred to by causing chloramine to interact with formaldehyde.

The manufacture of the new product referred to

containing basic aluminum acetate, then heated such as by ironing it, and finally coated or impregnated with a suitable varnish.

The method referred to, the application of cellulose acetate alone or combined with other varnishes as the varnish described herein.

In the method claimed, the employment of a varnish containing such materials as combine with the substances used to make the linen waterproof so as to form therewith an insoluble chemical combination as described herein.

"IMPROVED PROCESS FOR DYEING HAIRS, FURS, AND THE LIKE." British Patent No. 18,921/10. Patent of addition to 5,134/10. Actiengesellschaft für Anilinfabrikation, Berlin.

Also French Patent No. 413,877; described in Specification 5,134/10, wherein meta-amino-dimethyl-para-anisidine, or meta-amino-dimethyl-ortho-anisidine is substituted for the meta-diamino-anisol or meta-diamino-phenetol.

NON-INFLAMMABLE CELLULOID OR CELLULOID SUBSTITUTE. British Patent No. 26,657/09.

Claims: In the manufacture of non-inflammable celluloid or celluloid substitute, the process for the production of a base (which is soluble in chloroform, acetone, glacial acetic acid and other solvents so as to form transparent films) consisting in treating anhydrous cellulose acetate in the course of manufacture (but before precipitation of neutralization) with an acid either diluted or concentrated, other than sulphuric acid and glacial acetic acid, as hereinbefore described.

The admixture of base produced as hereinbefore described, with camphor or camphor substitute such as triphenyl phosphate or trinaphthyl phosphate, glycerine derivatives and oils with suitable solvents and filling bodies to form tough non-inflammable material, substantially as hereinbefore described.

The complete process for the manufacture of non-inflammable celluloid or celluloid substitute as hereinbefore described.

IMPROVEMENTS RELATING TO THE ARTIFICIAL PRODUCTION OF INDIA RUBBER OR CAOUTCHOUC. British Patent No. 15,299/09.

Claims: The treatment of material consisting of or containing certain substances of the terpene series, with natural rubber or latex containing micro-organisms, or cultures of the bacilli or enzymes obtained therefrom, substantially as and for the purpose specified.

The treatment of isoprene or its homologues or material containing the same, consisting in subjecting the isoprene or the like to the action of anaerobic bacilli obtained from natural rubber or latex, or other sources, or enzymes obtained with such bacilli, substantially as described and for the purpose specified.

Artificial rubber and the method of producing the same as hereinbefore described.

MANUFACTURE OF A BLUISH RED DYESTUFF SUITABLE FOR PREPARING LAKES FAST TO LIGHT. British Patent No. 22,289/10. Meister Lucius & Brüning, Hoechst.

Claims: The herein-described manufacture of a bluish red azodyestuff suitable for the preparation of color lakes which consists in combining diazotized 5-nitro-2-amino-1-benzylsulphonic acid with 2,3-oxy-naphthoic acid.

As a new product, a dyestuff consisting of a combination of diazotized 5-nitro-2-amino-benzylsulphonic acid with 2,3-oxy-naphthoic acid.

MANUFACTURE OF A NEW DISAZODYESTUFF. British Patent No. 17,614/10. Griesheim-Electron.

Claims: The herein-described manufacture of a disazodyestuff by combining the tetrazocompound of the dichlorodinitrobenzidine (which can be obtained by nitration of the meta-metal-dichloro-diacetylbenzidine and by splitting off the acidyl groups of the product) with two molecular proportions of betanaphthol in presence or absence of a substratum, with or without Turkey-red oil or another similarly acting material.

As a new article of manufacture the new dyestuff manufactured as above set forth.

IMPROVEMENTS IN DYESTUFFS OF THE INDIGO SERIES AND THE PRODUCTION THEREOF. British Patent No. 15,142/09. Levinstein, Ltd.

Claims: The process of producing blue vat dyestuffs containing arsenic and bromine, by treating with bromine, indigo in suspension in a suitable inert diluting medium in the presence of arsenic or arsenic acid or arsenious acid or their respective anhydrides as and at the temperatures hereinbefore described.

The process of producing blue vat dyestuffs containing arsenic and bromine described in the example hereinbefore given.

The process of producing blue vat dyestuffs described in the example hereinbefore given, but with the arsenic replaced by 6 parts of arsenious acid.

The process of producing blue vat dyestuffs described in the example hereinbefore given but with the arsenic replaced by 8.5 parts of arsenic acid.

Blue vat dyestuffs produced according to the process described above.

PROCESS FOR THE PREPARATION OF HALOGEN DERIVATIVES OF INDIGO COLORS. French Patent No. 412,642. Badische Anilin and Soda Fabrik.

Claims: Process for the production of salts of halogen derivatives of indigo colors, or their dehydro-derivatives or indigo-like colors having in their molecules an indoxyl nucleus or their dehydro-derivatives consisting in treating these substances with halogen or halogenization agents in the presence or absence of salts capable of combining with halogen acids with or without the addition of acids which may form salts with the free dehydro indigo substances.

Recently Granted German Patents.

- Modifications of Electric Cells for Use in the Hargreaves-Bird and Similar Processes.** Class 12h. No. 227,023. Applied for Nov. 30, 1906.
- Process for Manufacturing Photographic Papers and similar products.** Class 57b. No. 226,982. Applied for July 17, 1909.
- Process for Regulating the Development of Oxygen by Perborates.** Class 8i. No. 226,090. Applied for July 28, 1908.
- Process for Producing Stable Hydrosulfite, free of water of crystallization.** Class 12i. No. 226,220. Applied for Dec. 12, 1908.
- Process for Producing Sulfuryl Chlorid.** Class 12i. No. 226,218. Applied for Oct. 19, 1909.
- Process for the Production of Sulfuric Acids, in Towers, from sulfurous acid, by means of nitric acid.** Class 12i. No. 226,610. Applied for Sept. 22, 1908.
- Production of Sulfuric Acid Anhydrid by Means of the Contact Process.** Class 12i. No. 227,095. Applied for Oct. 2, 1909.
- Process for the Production of Sulfuric Acid by Oxidation of Sulfurous Acid by Means of Nitrogen Oxids.** Class 12i. No. 226,219. Applied for Jan. 3, 1909.
- Process for Producing Chemical Compounds from Mixtures of Gases.** (As SO_3 from $\text{SO}_2 + \text{O}$, etc.). Class 12g. No. 225,195. Applied July 24, 1906.
- Process for Working up Barium Chlorid and Strontium Chlorid for the Production of Chlorin and the corresponding hydroxids.** Class 12m. No. 227,096. Applied for July 7, 1907.
- Process for Generating Nitrogen Oxids in the Electric Arc.** Class 12i. No. 227,012. Applied for July 22, 1908.
- Process for the Continuous Production of Nitric Acid from Nitrates and Sulfuric Acid.** Class 12i. No. 227,377. Applied for Nov. 29, 1908.
- Process for the Production of Nitrogen Oxids by the Combustion of Nitrogen in a Generator.** Class 12i. No. 227,490. Applied for May 26, 1909.
- Apparatus for the Mechanical and Methodical Introduction of Slaked Lime into the Ammonia Distillation Apparatus.** Class 12k. No. 226,109. Applied for July 28, 1898.
- Process for Binding Nitrogen and Other Gaseous Bodies to Alkali or Earthy Alkaline Metals.** Class 12k. No. 227,320. Applied for Dec. 22, 1908.
- Process for the Production of N_2O and NO .** Class 12i. No. 226,867. Applied for Sept. 20, 1908.
- Process for the Purification of Graphite or Ores which were separated by the Simultaneous action of water, mineral oils and gases.** Class 1a. No. 227,431. Applied for Nov. 28, 1909.
- Process for the Production of Alkali Silicate (Water Glass) Solutions.** Class 12i. No. 226,791. Applied for Dec. 17, 1909.
- Process and Furnace for the Fusion of Ores.** Class 40a. No. 225,750. Applied for May 21, 1908.
- Process for the Treatment of Poor Ores which Contain Arsenic, Antimony and Sulfur.** Class 1a. No. 226,434. Applied for May 10, 1908.
- Process for the Production of Magnesium Carbonate and Other Magnesium Compounds.** Class 12m. No. 262,221. Applied for No. 23, 1909.
- Purification of Crude Copper by Fusion with Oxygen-Providing and Slag-Producing Oxids.** Class 40a. No. 227,622. Applied for Jan. 25, 1910.
- Process for the Working Up and Fusing of Products Containing Tin Resulting from the Electrolytic Determining of Tin Plate.** Class 40a. No. 227,209. Applied for July 11, 1908.
- Process for the Manufacture of Quartz Glass Objects.** Class 32a. No. 226,809. Applied for Dec. 1, 1908.
- Process of Water Purification by Means of Barium Carbonate.** Class 85b. No. 225,281. Applied for Feb. 7, 1909.
- Process for the Clarification of Sewage.** Class 85c. No. 226,430. Applied for June 28, 1908.
- Process for the Manufacture of Sodium Cyanid.** Class 12k. No. 227,780. Applied for April 19, 1910.
- Wool Degreasing.** Class 29b. No. 226,351. Applied for Jan. 1, 1910.
- Process for the Production of Cellulose Solutions which can be used for the production of artificial threads or films.** Class 29b. No. 227,198. Applied for Aug. 27, 1909.
- Contributions to the Theory of the Manufacture of Thorium Salts, I. The sulphate purification process.** Z. anorg. Chem., LXVII, pp. 266-92. (German.)
- Suggestions for Burning Difficult Clays.** Brick Pottery Trades J., XVIII, pp. 473-4. Oct. 1, 1910.
- The Differentiation of Artificial and Natural Silks.** A. HERZOG. Dresden, 1910. 75c. 78 pp. 50 photomicrographs. (German.)
- Tanning Agents and Dyes; Microchemical examinations (classification of the vegetable dyes and systematic summary of the color reactions of tanning agents with inorganic reagents).** L. E. CAVAZZA. Z. wiss. Mikros., XXVII, pp. 34-40. (German.)
- Handbook of the Lacquer and Varnish Industry.** F. SEELIGMANN and E. ZIEKE. Berlin, 1910. \$7.00. (German.)
- An Introduction to the Chemistry of Paints.** J. A. FRIEND. New York, 1910. \$1.20.
- Methods for the Determination of Glycerin.** Seifensieder Ztg., XXXVIII, p. 697, et seq. (German.)
- Chemical Technology.** G. RAUTER. 2d Edition. Leipzig, 1910; 144 pages. 20c. (German.)
- Electroanalysis.** F. FOERSTER. Z. Elektrochem., xvi, pp. 826-37. (German.)
- Handbook of Spectroscopy.** H. KAYSER. Vol. 5 and 6, completing the work. Leipzig, 1910. \$11.50. (German.)
- Dictionary for Photography and the Technic of Reproduction (Chemography, Heliogravure).** G. H. EMMERICH. Vienna, 1910. \$3.00. (German.)
- Analytical Chemistry of the Metalloids.** A. GUTBIER. Chem.-Ztg., XXXIV, pp. 985-6, 1007-8, 1017-18, 1029-30, 1038-40. (German.)
- Technical Application of the Nitrogen of the Air.** E. GEINSPERGER STEYR. 1910. Price, —. (German.)
- Some Attempts to Produce NO from air in the Electric Arc under Pressure.** F. HABER and W. HOLWECH. Z. Elektrochem., xvi, pp. 810-13. (German.)
- Rapid Determination of Carbon in Steel and Other Iron Alloys.** R. AMBERG. Chem.-Ztg., XXXIV, p. 904. (German.)
- Technologie of the compounds of Aluminium.** F. RUSS. Oesterr. Chem.-Ztg., [2] XIII, pp. 222-27. (German.)
- Results of the Examination of Copper and Copper Alloys.** Milt. Tech. Gewerbemus. Wien., [2] XX, pp. 94-114. (German.)

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF MARCH.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Acetanilid.....Lb.	20 ¹ / ₂ @	23
Acetone (drums).....Lb.	14 @	14 ¹ / ₂
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	2.15 @	2.35
Acetic Acid (28 per cent.).....C.	1.60 @	1.72 ¹ / ₂
Acetate of Lead (gray).....C.	1.75 @	1.80
Acetate of Lime (brown, broken).....Lb.	7 ³ / ₄ @	8
Aniline Oil.....Lb.	11 ¹ / ₂ @	11 ³ / ₄
Benzoic Acid.....Oz.	11 ¹ / ₄ @	12
Boric Acid, crystals.....Lb.	7 @	7 ¹ / ₂
Carbon Tetrachloride (in drums).....Lb.	8 ¹ / ₈ @	12
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (in drums).....Lb.	9 @	11
Citric Acid (domestic).....Lb.	38 ¹ / ₂ @	39
Camphor (refined in bulk).....Lb.	.. @	46
Dextrine (imported potato).....Lb.	5 ¹ / ₂ @	7
Dextrine (domestic corn).....C.	2.12 @	2.28
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 ¹ / ₂ @	9 ¹ / ₂
Glycerine (dynamite).....Lb.	25 @	25 ¹ / ₂
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7.20 @	7.75
Pyrogallie Acid (bulk).....Lb.	1.00 @	1.05
Paraffine (crude) 120 @ 122 m. p.....Lb.	3 @	3 ¹ / ₄
Paraffine (refined), domestic 120 @ 122 m. p.....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	1.37 @	1.53
Starch (potato).....Lb.	4 @	5 ¹ / ₄
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 ⁷ / ₈ @	5 ¹ / ₄
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	29 ¹ / ₄ @	29 ¹ / ₂

Inorganic Chemicals.

Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (in drums) 16°.....Lb.	2 ³ / ₄ @	3
Ammonium Chloride, gray.....Lb.	6 ¹ / ₃ @	6 ¹ / ₄
Arsenic, white.....Lb.	2.00 @	2.10
Ammonium Carbonate, domestic.....Lb.	8 @	8 ³ / ₄
Aluminum Sulphate.....Lb.	9 @	10 ³ / ₄
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2.25
Barium Nitrate.....Lb.	5 ¹ / ₂ @	6 ¹ / ₂
Borax, crystals in bags.....Lb.	3 ¹ / ₂ @	4
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.25 @	1.30
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 @	4 ¹ / ₄
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	90 @	92
Chalk (light precipitated).....Lb.	4 ¹ / ₂ @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (in bags).....C.	62 ¹ / ₂ @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 @	8 ¹ / ₂
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	81 @	84
Nitric Acid, 36°.....Lb.	3 ⁷ / ₈ @	4 ¹ / ₄
Nitric Acid, 42°.....Lb.	4 ⁷ / ₈ @	5 ¹ / ₄

Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25
Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 ¹ / ₂ @	12
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals, f. o. b. works.....Lb.	8 ¹ / ₄ @	9 ¹ / ₄
Potassium Nitrate (crude).....Lb.	4 ³ / ₄ @	5
Potassium Bichromate, 50°.....Lb.	7 ³ / ₈ @	7 ³ / ₄
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	75 @	77
Salt Cake (glass-makers).....C.	63 ¹ / ₃ @	78 ¹ / ₂
Silver Nitrate.....Oz.	33 ¹ / ₃ @	36
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 ¹ / ₃ @	5
Sodium Chlorate.....Lb.	8 ¹ / ₄ @	9 ¹ / ₄
Sodium Bicarbonate (English).....Lb.	2 ³ / ₄ @	3
Sodium Bichromate.....Lb.	5 ⁵ / ₈ @	5 ³ / ₄
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 ¹ / ₂
Sodium Hydroxide, 60 per cent., f. o. b. works.....C.	1.85 @	1.90
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.	7 @	10
Sodium Nitrate, 95 per cent., spot... C.	.. @	2.10
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 ³ / ₄ @	10
Strontium Nitrate.....Lb.	7 ³ / ₈ @	7 ³ / ₄
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	90 @	1.00
Talc (American).....Ton	15.00 @	25.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	12 ¹ / ₂ @	13
Tin Oxide.....Lb.	45 @	47
Tin Chloride (36°).....Lb.	11 @	11 ¹ / ₂
Zinc Chloride (granulated).....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Zinc Sulphate.....Lb.	2 ¹ / ₄ @	2 ¹ / ₂
Zinc Dust.....Lb.	6 ³ / ₄ @	7

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 ¹ / ₄
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	10 @	20
Corn Oil.....C.	6.68 ¹ / ₃ @	7.73 ¹ / ₃
Cottonseed Oil (crude), f. o. b. mill... Gal.	42 @	43
Cylinder Oil (light, filtered).....Gal.	19 ¹ / ₃ @	20
Japan Wax.....Lb.	9 ¹ / ₄ @	9 ¹ / ₂
Lard Oil (prime winter).....Gal.	95 @	1.05
Linseed Oil (raw, city).....Gal.	96 ¹ / ₃ @	97 ¹ / ₃
Linseed Oil (double-boiled).....Gal.	98 @	99
Paraffine Oil (high viscosity).....Gal.	23 ¹ / ₂ @	24
Rosin Oil.....Gal.	— @	36
Spindle Oil, No. 1.....Gal.	14 @	14 ¹ / ₃
Stearic Acid (double-pressed).....Lb.	11 @	11 ¹ / ₂
Sperm Oil (bleached winter) 38°.....Gal.	83 ² / ₃ @	86 ² / ₃
Tallow (acidless).....Gal.	63 @	70
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum.....Lb.	21 @	21 ¹ / ₂
Antimony.....Lb.	7 ¹ / ₄ @	7 ³ / ₄
Bismuth.....Lb.	1.80 @	1.90
Copper (electrolytic).....Lb.	12 ³ / ₅ @	12 ⁶ / ₅
Copper (lake).....Lb.	12 ¹ / ₂ @	12 ³ / ₈
Lead.....Lb.	4.4 @	4.42 ¹ / ₂
Mercury.....Lb.	61.3 @	61.5
Nickel.....Lb.	40 @	45
Platinum (refined).....Oz.	— @	41.00
Silver.....Oz.	52 ³ / ₈ @	53
Tin.....Lb.	41 ¹ / ₄ @	42
Zinc.....Lb.	5.5 @	5.6

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EDITORIALS

THE SYNTHESIS OF INDIA RUBBER.

The synthesis of rubber dates back to the observations of Bouchardat (1879) and of Tilden (1882) that isopren, a definite compound C_5H_8 (boiling point $37-38^\circ C.$) isolated from the products of the dry distillation of india rubber, was the only substance thus obtained, which could be polymerized again into india rubber. According to these investigations isopren undergoes such a change after treatment with hydrochloric acid followed by distilling off the volatile by-products of the reaction with steam.

These experiments, however, have never been duplicated and the products obtained have never been satisfactorily examined so as to furnish positive proof that they were in fact india rubber. On the contrary Harries, one of the greatest authorities in this field of chemistry, after years of research, stated emphatically that the above results could not be confirmed by him and his pupils.

In order to allow impartially to each of the various investigators his proper share, we quote from an interview granted in 1908 by Prof. Tilden to a representative of the *India Rubber Journal*,¹ and from a lecture delivered March 12, 1910, by Prof. Harries,² leaving it to the reader to draw his own conclusions from these authoritative publications as to the part which the different investigators had in the historical development of the solution of the problem of the synthetic production of rubber. The interview states: "The writer recently had an opportunity of talking the subject over with Prof. Tilden (now Dean of the Royal College of Science, London) who, as everybody knows, achieved some success in the synthetical production of rubber. An account of what he really did in days gone by will not be out of place at this

juncture. The details can be seen and studied by our readers in the transactions of Scientific Societies and records of chemical journals."

"Prof. Tilden's first note on the spontaneous conversion of isopren into caoutchouc was read before the Birmingham Philosophical Society, May 18, 1892. He then explained that 'isopren' is a hydrocarbon which was discovered by Greville Williams many years ago among the products of the destructive distillation of india rubber. Later, in 1884, it was observed by myself among the more volatile compounds obtained by the action of a moderate heat upon oil of turpentine and other terpenes. It is a very volatile liquid boiling at about 36° ."

"Bouchardat observed that when isopren is heated to a temperature near 300° it gradually polymerizes into a terpene, which he called di-isopren, but which is now called di-pentene. This compound boils at 176° . A quantity of colophene similar to that which is produced by the action of heat upon turpentine is formed at the same time. When isopren is brought into contact with strong acids, aqueous hydrochloric acid, for instance, a small portion of it is converted into a tough, elastic solid, which has been examined by G. Bouchardat and by myself. It appears to be true india rubber."

"Specimens of isopren were made from several terpenes in the course of my work, and some of them I have preserved. I was surprised a few weeks ago at finding the contents of the bottles containing isopren from turpentine entirely changed in appearance. In place of a limpid, colorless liquid, the bottle contained a dense syrup in which were floating several large masses of a solid of a yellowish color. Upon examination, this turned out to be india rubber. The change of isopren by spontaneous polymerization has not, to my knowledge, been observed before. I can only account for

¹ *India Rubber Journal*, October 5, 1908.

² *Gummi-Ztg.*, March 18, 1910.

it by the hypothesis that a small quantity of acetic or formic acid had been produced by the oxidizing action of the air, and that the presence of this compound had been the means of transforming the rest. The liquid was acid to test paper, and yielded a small portion of unchanged isopren."

"The artificial india rubber, like natural rubber, appears to consist of two substances, one of which is more soluble in benzine or carbon bisulphide than the other."

"A solution of the artificial rubber in benzine leaves on evaporation a residue which agrees in all characteristics with a similar preparation from para-rubber."

"The artificial rubber unites with sulphur in the same way as ordinary rubber, forming a tough, elastic compound. It is obvious that compounds such as these, containing doubly-linked carbon, may polymerize in a variety of ways; and, in the present condition of our knowledge even of isopren, it would be idle to speculate as to which out of the numerous possible arrangements would correspond to the constitution of caoutchouc."

In a letter once published in the *Kew Bulletin*, Prof. Tilden stated that: "As you may imagine, I have tried everything I can think of as likely to promote the change, but without success. The polymerization proceeds very slowly, occupying, according to my experience, several years, and all attempts to hurry it result in the production, not of rubber, but of 'colophen,' a thick, sticky oil, quite useless for the purpose to which rubber is applied."

Professor Tilden further states: "The conversion of isopren into rubber occurs, so far as observed, under two conditions."

"(1) When brought into contact with strong aqueous hydrochloric acid or moist hydrogen chlorid gas.

"(2) By spontaneous polymerization.

"In the former case the amount of rubber produced is small, as it is only a by-product attending the formation of the isopren hydrochlorides, which are both liquid. In the latter case the process occupies several years. Of course, many attempts were made by me to hasten the process, but it was found that contact with any strong reagent, such as oil of vitriol, pentachloride of phosphorus, and others of a milder character, led only to the production of a sticky "colophene" similar to the substance which results from the polymerization of the terpenes, and after a course of experiments which were carried on for about two years, I was reluctantly obliged to abandon the subject. It is, however, a question whether the process could be made commercially productive even if a suitable reagent could be found to effect the transformation, because the yield of isopren from turpentine is very small, probably not exceeding 10 per cent. under favorable conditions. In my experience it was less. If isopren were obtainable at a low cost from the other sources it might be found possible to utilize the hydrochloric acid process, though I doubt it."

Prof. Harries states: "Caoutchouc even in a high vacuum cannot be distilled without decomposition. If it is heated in a retort, the most varied products

go over, some of them beginning to boil at 25°, and some of them boiling at 300° C. and even above. Only two fractions of these products of distillation have been studied more carefully, namely, the one boiling at 30-40°, and the one boiling at 160-170°. According to Wallach the latter fraction contains dipentene while the former consists of isopren, dimethylallene and dihydroisopren. These constituents were mainly investigated by Ipatieff, who showed that pure isopren can only be produced in a most circumstantial way. The constitution of isopren was proven by Euler and Ipatieff. Isopren was known for a long time, although it is obtained only in small quantities on distilling caoutchouc. I ascertained that 1½ kg. of good caoutchouc furnished only 35 grams of an isopren fraction boiling at 33-34°. Although only so little is obtained the bold conclusion was arrived at already at an early date that isopren not only stands in near relation to caoutchouc, but was more closely related to it than all the other products of distillation."

"W. A. Tilden in 1882 was the first to observe that isopren can be polymerized. By saturating the isopren fraction with hydrochloric acid gas "india rubber-like masses" were said to separate. Later Tilden found that isopren, which he had obtained by conducting turpentine through tubes heated to a glow, also polymerized and furnished substances which he declared were caoutchouc. He attributed this reaction to the presence of a small quantity of acid, which had been formed during the pyrogenous process. Wallach and also Ipatieff remarked briefly that isopren polymerized when exposed to light. Later Klages in a lecture in Heidelberg declared that according to his experience it was excluded to transform isopren into caoutchouc."

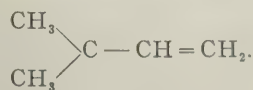
"During a period of seven years with the coöperation of many of my collaborators, I tried to duplicate the reactions of Tilden, but have never been able to confirm his results. Other investigators also advised me that they had never been able to obtain the products described by Tilden. I show you here a substance prepared three months ago by saturating isopren with hydrochloric acid gas. Apart from its brownish color, it has remained unchanged. If isopren is treated with an organic acid and allowed to stand, no material changes are observed even after many months; formic acid however acts at once, but produces only a resin. It is therefore evident that Tilden must have encountered quite accidentally conditions under which polymerization of isopren was effected, but—what of course is of the utmost importance—he did not adduce proofs that he had actually produced caoutchouc; for as I am going to show later, isopren furnishes all kinds of substances on polymerization, and many products may be characterized as "india rubber-like," which bear only very little relation to caoutchouc. As a matter of fact isopren, on standing for a long time in the presence of air, becomes thick, but this is not due to polymerization. A peroxide is formed, which on heating is very explosive. For a long time my experience was the same as that of

Klages. A new incentive to take up again the study of the subject came last summer, when upon the recommendation of Prof. Hempel a large English house sent me a sample with the request to ascertain whether it was real caoutchouc. The substance had been prepared according to a patented process of a Dr. Heinemann, in England, consisting in conducting, simultaneously through a glowing tube acetylene, ethylene and chlormethyl. In this way isopren was first produced and immediately converted into caoutchouc by polymerization. I did ascertain as a matter of fact that the substance was caoutchouc, it furnished a levulinaledehyde with ozone and a nitrosite with nitrous acid, and its appearance was that of para-rubber. This result was communicated to the firm with the caution however to ascertain whether the material tested had been really made according to the process of Heinemann."

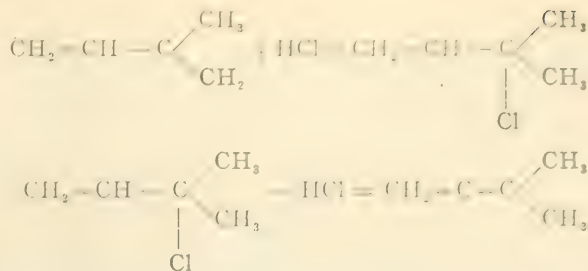
"For some time I experimented according to the directions of the patent, but neither myself nor any other chemist could reproduce the results described. If, by following this process, isopren and caoutchouc can really be produced it must be done under specific conditions which should have been described in the specification, and should any one actually ascertain the character of these conditions, I would consider him an independent inventor. It is my belief, however, that the process is inoperative. At any rate, these experiments caused me to take up again the synthesis of isopren and its polymerization, when in the beginning of November, 1909, the Elberfelder Farbenfabriken at the request of Prof. Duisberg sent me some samples of artificial caoutchouc obtained from isopren according to a process discovered by Dr. Fritz Hofmann. I could prove beyond a shadow of a doubt that these samples were real caoutchouc and therefore the examined substance was the first synthetic caoutchouc ever obtained."

From the above data, it becomes obvious that the problem of synthesizing india rubber is identical with that of the synthesis of isopren and its polymerization into india rubber. Under the circumstances, the constitution of isopren becomes of paramount importance and may be advantageously discussed at some length.

Tilden¹ already concluded that isopren had the constitutional formula of $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$, giving it the name of beta-methylcrotonylene. But he did not support his theory by experiments, and it was Gadziatzky² who carried out the first researches which partially confirmed the Tilden formula. This author prepared from the monochlorhydrate of isopren a tertiary alcohol, dimethylvinylcarbinol,



Subsequently³ he found that isopren is converted into an isomeric dimethyl-allene if it is heated with weak alcoholic hydrochloric acid.

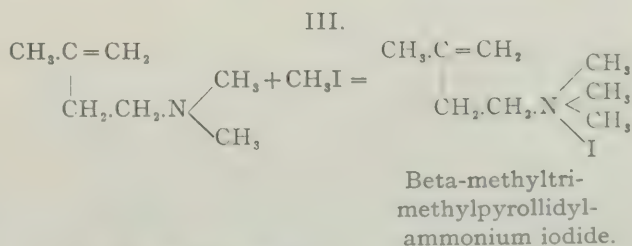
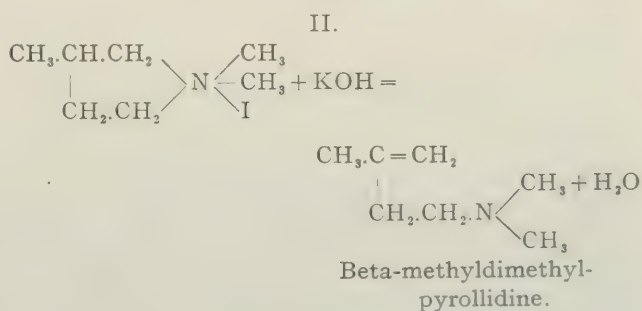
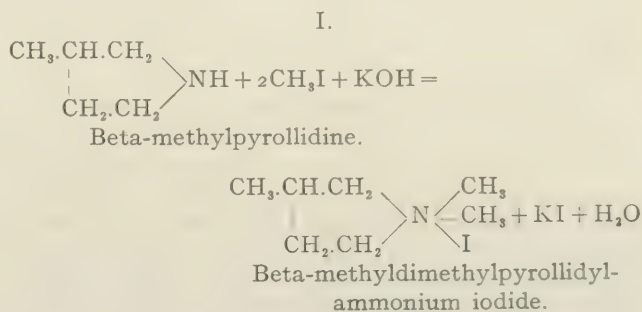


These experiments, however, furnished only liquids which were liable to decomposition on distillation, and altogether did not possess sufficiently definite properties.

Mokiewsky⁴ produced the first crystalline body by the action of hypochlorous acid upon isopren.

Ipatiev and Hittorf² experimented with dihydrobromides of the formula $\text{C}_5\text{H}_{10}\text{Br}_2$ and contributed largely to the experimental proof of the constitution of isopren, which however was finally supplied by Euler³ who produced beta-methyldivinyl synthetically and showed it to be identical with isopren.

Basing his experiments on the reaction published by Ciamician and Magnaghi⁴ who prepared divinyl from dimethylpyrrolidyl-ammonium iodide on treatment with caustic potash, he transformed beta-methylpyrrolidine into beta-methyldivinyl as follows:



¹ Jour. Russ. Chem. Ges., 27, 516.

² Jour. prakt. chem., [2] 55.

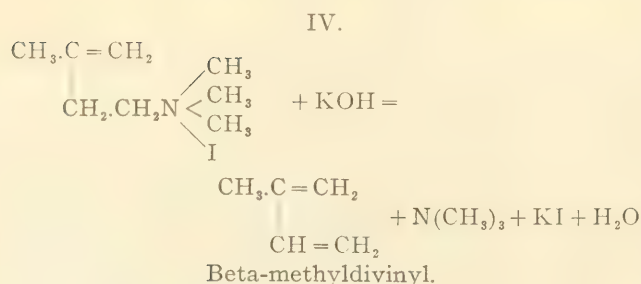
³ Ibid., [2] 57, 131.

⁴ Ber., 18, 2080.

¹ Bull. soc. chim., [2] 47, 168.

² Chem. News, 46, 129.

³ Jour. Russ. Chem. Ges., 20, I, 706.



The beta-methyldivinyl which is furnished by these reactions is identical with isopren and the steps of the process furnish absolute proof of the constitution of isopren, namely $\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$.

As stated above, the main problem with which we have to deal in the synthesis of india rubber is the economical production and the polymerization of isopren. If, however, the constitution of isopren as a diolefin with two double valencies is considered, another line of research suggests itself as a matter of course. Undoubtedly the polymerization to india rubber takes place at the double links of the chain $\text{C}=\text{C}-\text{C}=\text{C}$, and if such is the case all hydrocarbons with such double links ought to furnish india rubbers on polymerization. If this proves to be correct we ought to be able to produce by synthesis not only the ordinary india rubber which is a methyl derivative, but also the methyl-free mother substance of india rubber and all kinds of "alkyl" and "aryl" india rubbers from homologues, etc., of isopren.

Accordingly 1,3-butadien, which is the simplest member of this series, $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, ought to polymerize into the mother substance of india rubber or "Nor-caoutchouc," a name proposed by Harries because the term "caoutchouc" itself has already been appropriated for the methyl derivative furnished by nature; therefore the methyl-free mother substance, to be synthesized, should bear the prefix "Nor" attached to the name under which the natural product is known.

In other words, a "Nor" substance is the synthetic, methyl-free, simplest form or mother substance of a series of bodies, the methyl derivative of which occurs in nature.

Consequently higher homologues of isopren, for example, the 2,3-dimethyl-1,3-butadien, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}_2$, should give a methyl india rubber and so on. What an endless vista of homologous and analogous rubbers opens itself before the eyes of the imaginative research chemist!

How much of these speculations and theories, or whether anything at all, has become a source of commercial success does not appear from the literature. But the Patent Offices are already reaping a huge harvest from the real and imaginary inventions in this branch of synthetical chemistry.

Any number of patents have been applied for and many have been already published especially by the English Patent Office. Of what value they are is beyond our judgment!

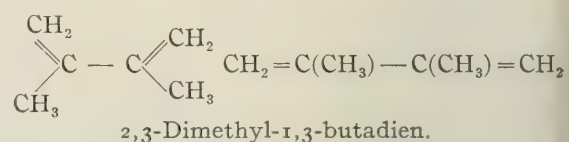
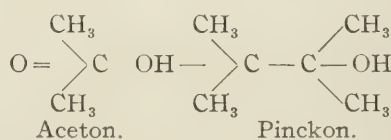
We shall, however, append here a few applications

as we found them recorded in a recent article in the new journal, "Kunststoffe," 1911, p. 65.

In a German patent application of November 29, 1909 (British patent 15,254, June 25, 1910), the Elberfelder Farbenfabriken describe the production of "Nor" caoutchouc by heating erythren (butadien) with or without the addition of reagents which facilitate polymerization. Among the various directions, we find the following: Erythrene dissolved in benzol is heated for ten hours to 150° , or erythrene condensed at low temperature (ether-carbonic acid) is kept in an autoclave at $90-100^\circ$ for four days. In both cases the solvents, unreacted upon starting material, and by-products are distilled off (*in vacuo* or by steam) and caoutchouc-like masses resembling india rubber remain as a residue.

French patent of the Badische Anilin- & Soda-Fabrik 417,170, June 15, 1910, describes the polymerization as follows: Isopren is heated for twenty hours to about 120° , and erythren for ten hours to 150°C ., or isopren with an addition of 10 per cent. of its weight of concentrated alcoholic caustic soda lye is heated to 100° for a sufficiently long time; after distilling off unreacted-upon isopren, caoutchouc is either dissolved in benzol and precipitated with alcohol or kneaded into a compact mass.

British patent 14,281 of 1910 to the Badische Anilin & Soda-Fabrik describes the polymerization of 2,3-dimethyl-1,3-butadien, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}_2$. This hydrocarbon had already been investigated by Kondakow.¹ It is obtained from acetone by reduction; the pinacon which is first formed is converted into the diolefin by splitting off the water.



The Badische Anilin- & Soda-Fabrik states that if 2,3-dimethyl-1,3-butadien be heated, either a one, or with an indifferent agent, such, for instance, as water, or a solution of common salt, or alcohol, or ether, or benzene, a product resembling caoutchouc is obtained in better yield and in purer form than is obtainable according to the method described by Kondakow, and moreover, the product of the present invention differs from that of Kondakow in being insoluble in alcohol. They can also obtain a product with similar properties by carrying out the heating in the presence of an aqueous solution or suspension of a base or of a salt which acts as a base, and in this case a small proportion of alcohol may be present without materially affecting the course of the reaction, but if a large proportion of alcohol be present the desired results are not obtained. As instances of sub-

¹ Jour. prakt. Chemie, Neue Folge, 62, 175-176.

stances which can be used in carrying out this invention, the alkalies, the hydroxides of the alkaline earth metals, and salts of an alkaline reaction (such, for instance, as the alkaline carbonates) are mentioned.

The following are given as examples of how this invention can be carried into practical effect, but the invention is not confined to these examples. The parts are by weight.

EXAMPLE 1.

Heat together equal quantities of 2,3-dimethyl-1,3-butadien and water in an autoclave for sixty hours at about 100° C. On distilling off any unaltered initial material in a current of steam, a white elastic substance, possessing the typical properties of caoutchouc, is obtained. It is soluble in benzene and is precipitated, in an unaltered condition, from the benzene solution by means of alcohol.

Instead of water in this example, a 10 per cent. solution of common salt or a solution of any other suitable indifferent salt can be employed and, if desired, a higher pressure can be obtained by passing an indifferent gas (such, for instance, as nitrogen) under pressure into the autoclave.

EXAMPLE 2.

Heat 2,3-dimethyl-1,3-butadiene in an autoclave for sixty hours at from 90–100° C. and work up the product as described in the foregoing example 1.

2,3-Dimethyl-1,3-butadien can also be caused to undergo polymerization by heating it in admixture with, for instance, equal quantities of other alcohol or benzene.

EXAMPLE 3.

Heat together equal parts of 2,3-dimethyl-1,3-butadien and caustic soda of 14 per cent. strength, for eighty hours in an autoclave at 100° C. On distilling off any unchanged initial material with steam, a substance resembling caoutchouc is obtained.

In a similar manner, either stronger or more dilute caustic alkali can be employed, or aqueous alcoholic alkali containing say 20 per cent. of alcohol, but preferably less, can be used.

Alkali carbonate, or ammonia, or an earth alkaline hydroxide can be used instead of the caustic alkali.

The india rubber which is thus produced might be called methyl caoutchouc. Thus we already know the series:

'Nor-caoutchouc,'	'Caoutchouc,'	'Methylcaoutchouc,'
polymerized	polymerized	polymerized
erythren.	isopren.	dimethylbutadien.

The most interesting of all descriptions yet published is a new German patent application (F. 29,898 Kl 39 b) of the Elberfelder Farbenfabriken (postscript of article in *Kunststoffe*) which directs polymerization under the following conditions: Heating in an autoclave to 150° for twenty-four hours, heating twelve hours to 200°, eight days to 90–100°, heating to 35° for three months in a closed vessel. As agent of polymerization formic acid and creosote may be

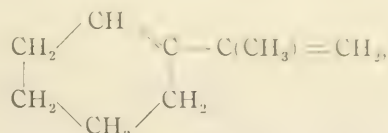
employed. Besides the diolefins already mentioned, the following hydrocarbons are polymerized into caoutchouc.

$(CH_3)CH=CH-CH=CH_2$ furnishes an isomer of natural caoutchouc.

$(CH_3)_2CH=CH-CH=CH_2$ furnishes an isomer of the above methyl caoutchouc.

$(CH_3)_2CH=CH-CH=C(CH_3)_2$ furnishes a trimethylcaoutchouc.

And finally—which is a reaction of the very greatest importance—the hydrocarbon, isopropenylcyclohexen, is polymerized to a caoutchouc,



furnishing a cyclohexen caoutchouc.

We also wish to mention Prof. Harries' method of polymerization of isopren as described by him in the lecture referred to above. Isopren is heated with glacial acetic acid in a closed tube to a little above 100° C. He finds that isopren from caoutchouc is not as easily polymerized as synthetic isopren and states that his conditions of reaction must be strictly adhered to, otherwise no isopren is formed, but instead a resinous, oily mass.

Harries identified his product as synthetic caoutchouc as follows: A sample was ozonized in a chloroform solution, the resulting ozonide was split up by water and half of the theoretical quantity of levulin-aldehyde recovered. On treatment with nitrous acid, the nitrosite decomposing at 167° C., was easily and quantitatively obtained, bromine gave the tetrabromide. He claims that the synthetic caoutchouc is as tough and elastic as the natural product; it is of light brown to whitish color.

As a curiosity we might here mention British patent 15,299 of 1909, with the following claim:

The treatment of isoprene or its homologues or material containing them, consisting in subjecting the isoprene or the like to the action of anaerobic bacilli obtained from natural rubber or latex or from other sources or enzymes obtained with such bacilli.

All the publications quoted thus far refer to the polymerization of only such diolefins which are already known in chemical literature, and the preparation of which is generally extremely difficult and exceedingly expensive. There seems no doubt that cheap methods for their production will be discovered before long and perhaps have already been found. The patent literature on this point is very scant and we are able to record only the following specifications:

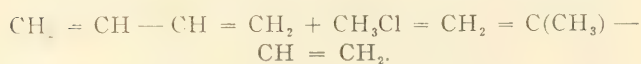
In English patent 27,908 of 1909 Woltereck describes the production of isopren by conducting the vapors of turpentine over iron at temperatures of 550–600° C. (not through a glowing tube as Tilden did).

Heinemann, British patent 21,772 of 1907, French patent 394,795, Belgium patent 210,979, first forms

1,3-butadien from acetylene and ethylene at dark glowing heat,

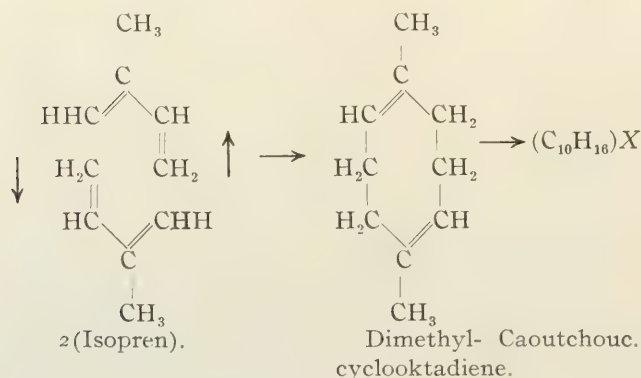


Then he allows chlormethyl to act on the butadien,

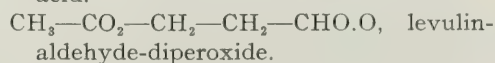
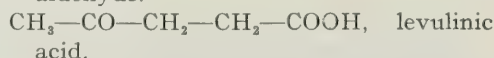
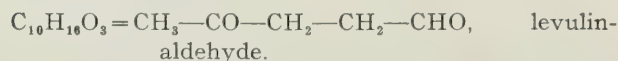


It is interesting to note that in spite of Harries' annihilating criticism of Heinemann's process, this inventor advertises now in the chemical journals that he is ready to furnish isopren in any quantity.

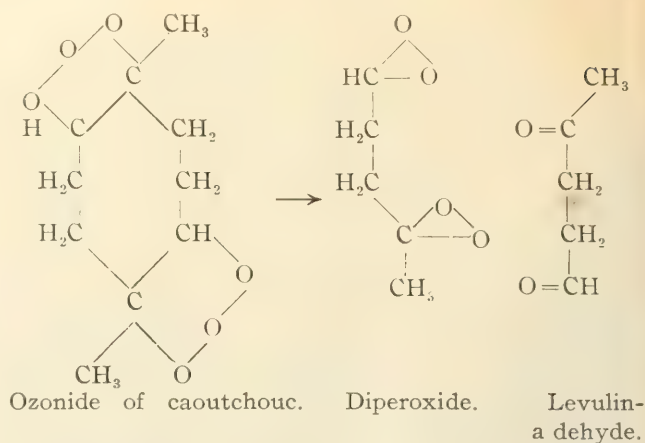
It will perhaps prove of interest to refer to the most modern theory on the polymerization of isopren and the constitution of caoutchouc. Harries claims that isopren first furnishes dimethylcyclooctadiene, which then polymerizes to india rubber, as shown by the following formula:



Caoutchouc is a hydrocarbon of the empirical formula $\text{C}_{10}\text{H}_{16}$, it is optically inactive and therefore has no asymmetric carbon in its molecule. On bromination it absorbs 4 atoms of bromine, therefore it contains 2 ethylene groups. Treated with ozone in chloroform solution, 2 molecules of ozone are absorbed. Since this ozonide is readily soluble, its molecular weight can be easily ascertained, it is $\text{C}_{10}\text{H}_{16}\text{O}_6$. This formula shows that the addition of ozone is preceded by a depolymerization of the large molecule. On boiling this ozonide with water, it is decomposed into levulin-aldehyde, levulinic acid and a crystallized substance which Harries considers to be levulin-aldehyde diperoxide.



This decomposition proves that the ozonide of caoutchouc contains an 8-carbon ring, because ozone enters the molecule at the ethylen groups and on splitting the molecule, the nucleus is broken at the place where the ozone was added and oxygen-containing products, aldehyde and acid are formed:



We hope soon to again take up this subject and give a review of all publications which describe the various processes of producing diolefins.

SUGGESTIONS AS TO PUBLIC SAFETY.

The appalling loss of life from the explosion of the boilers of the Staten Island ferryboat *Westfield* resulted in a very great improvement in the official oversight of steamboat boilers by the United States Government officials having jurisdiction over the navigable waters of the country.

The General Slocum horror in which more than one thousand persons were either burned or drowned from a single steamboat resulted in more care of the fire hazards on steamboats.

Boiler explosions in the early days of steam engineering caused much improvement in the inspection of steam boilers, which is still carried on.

The Tarrant explosion in New York brought about an improvement in the warehousing of drugs and chemicals.

The Park Avenue explosion within 100 yards of the Chemists' Building in New York caused the dynamite hazard in particular to be better watched and other dangers of explosion to be also subject to official control with a view to minimizing them.

All of these laws and regulations are on the statute books of almost all cities. More are sure to be added and more it is hoped are to be reconsidered, strengthened, codified and receive sanction by vigorous enforcement. But after all these legal activities are at work can we say, as the watchman of the night, "All's well?" Indeed we cannot and we know it. Tomorrow morning we may awake to find recorded some awful disaster, some harrowing story of suffering and death to crowds, and on due consideration of the initiating conditions of the accident we shall not be surprised.

Then let us ask ourselves why this is so. Obviously it is on account of human weakness. This manifests itself in forgetfulness, in ignorance, indifference, carelessness and corruption. It would seem then that, next to honesty, vigilance would be the remedy, vigilance of officials and vigilance of the citizen body. The former would be stimulated by the latter and the

Address delivered before joint meeting of the American Electrochemical Society, April 7, 1911.

latter can be stimulated by an examination of conscience. (Vigilance presupposes foresight.)

I have for many years been studying the hazard of explosives. Undoubtedly the precautionary measures of the past have produced much safety in the very midst of excessive danger. I have no mental conception of the weight and energy of the dynamite and fulminate caps used in New York for the last ten years to rend the rocks that come out of the bowels of this city for the subway, the Pennsylvania cut and the Grand Central improvement, etc., but I am certain that had not the precautions been taken whose enforcement followed the Park Avenue explosion so many and so terrible would have been the accidents that the works would have terminated by public clamour.

If the violation of law by a steamship company leaving explosives in large quantity, uncared for, on a dock is relaxed, then indeed the hazard is unsupportable. If the vigilance which the firemen have exercised in our theaters, many and many a time extinguishing a slight blaze, is not to be applied to factories and buildings housing five thousand people per acre, then indeed we would have to be always prepared for the usual report of a holocaust in the morning papers.

But desuetude and laxity bring peril in the administration of public office, even where corruption may not have penetrated. To provide and enforce such vigilance I have come to the conclusion that in the storage of dangerous things, in the prosecution of hazardous construction, in the carrying on of risky business, and in all of our twentieth century activities in the very heart of crowds, we should provide for vigilance by forming a new kind of Committee on Public Safety. Let this be constituted by our foremost civic bodies, such as the Chamber of Commerce, let membership in it be a valuable reward to active, thoughtful, honest citizens of eminence, who serve gratuitously, let them have funds from public subscription aided by grants from philanthropic foundations, and prescribe as their duty the oversight of a special bureau devoted to considerations of how to insure public safety, its watchword being "*foresight*." It could maintain a force of engineers engaged in surveying the city for possible dangers to the public not already patent to officials, or not sedulously provided against by them. For example, if there is any hazard growing into an abuse it could inform the right official and see to the enactment of laws to end it. If there is laxity in enforcing old laws public sentiment could be aroused to stimulate the negligent official. At parades and public festivities it could aid the police, the Building Department, the Fire Department without interfering or dictating and give each of these due credit for their own good work, such as was manifested on land and water during the Hudson-Fulton celebration. The excellent purposes of the National Highways Association could be aided by this Committee on Public Safety. The clashing of different public commissions, departments or bodies could be reconciled by the wisdom of the counselors on this committee.

In the work of prevision or foresighting of danger and making preparations against disaster certain objects of study could be taken up which are nobody's business now because they are everybody's business. We may be certain that the fire and panic risk in factory buildings is going to be well considered now for a period, but we should have had a body working on the problem before this, and ready in the future to see that to-day's lessons are not forgotten. Such objects of study as I have stated as everybody's business and hence overlooked in the confusion are the possibilities in the subway which include dangers from gas, from electricity, from wrecks, etc., possibilities from the storage, as now practiced, of enormous quantities of dynamite at Black Tom in our harbor. The possibilities of disasters in old buildings or buildings under construction, the possibilities of disasters on our waters where perhaps the combustible and panic risks on steamboats might be drifting back to old conditions or dangers on our bridges could be studied, and lastly the duties of the commission would of course cover all considerations regarding factories, theaters and schools.

The problems are unique. City officials have little time for problems other than their daily work affords them. Somebody else should consider problems of public safety, and officials will be only glad enough to apply the results. To be brief, I maintain that public safety can be only reasonably well assured by endowing some group of men with eternal vigilance and foresight and powers of investigation, and trusting them to tell us where danger lurks through newly discovered hazards or through official laxity or turpitude; and all of this in the field of fire, flood, explosion, transportation and construction.

CHARLES F. MCKENNA.

COLD STORAGE.

The preservation of foodstuffs so that the surplus created during seasons of plenty could be distributed throughout the year and the fresh products of one country shipped to another was at one time impossible. The use of chemical preservatives which arrested decomposition served, in a measure, to supply the need, but this doubtful method of retarding the natural spoilage of foodstuffs has given way almost entirely with the development of methods of refrigeration which make it possible for foods of every character to be placed in cold storage and there held for considerable periods without apparent change in composition or structure. Cold storage is simply the placing of foodstuffs in rooms kept at a sufficiently low temperature to hold the goods in normal condition until such time as these are needed for consumption. This temperature varies from a point several degrees above freezing to zero and below. Certain goods, such as fruits which can not well be frozen, can be kept without any spoilage for months at a temperature of about 34° F., while butter and meats are stored at a temperature ranging from below zero to freezing. Poultry is usually stored at a temperature

varying from 0-25°. Cheese, supposed by manufacturers to cure or ripen in storage, is usually held at a temperature slightly above freezing. Cold storage at suitable temperatures undoubtedly improves certain foodstuffs up to a certain point. This is especially true in the case of fresh meats, poultry and fruits. Other products do not improve in storage and after a time begin to deteriorate even when kept at temperatures which inhibit to a large extent the ordinary processes of fermentation and decay.

The investigations of the United States Department of Agriculture on the effect of cold storage on eggs, poultry and game have been carefully worked out and have developed much data which throws a new light upon the results of storage at low temperatures. In general the results of the studies show that cold storage when properly used is a very valuable improvement in the methods of the conservation and distribution of the food supply and that the term "cold storage" as applied to foods is in no sense a mark of inferiority or low grade.

It is true that time limits are well established beyond which goods should not be kept in storage, and that if such foods as eggs, fish or poultry are held for a longer period deterioration, at first slight and later marked, takes place. But such time limits are sufficiently long to carry the products until the natural season of scarcity is past and in fact carrying charges, insurance and interest on the money invested does not, except under most unusual conditions, make it profitable for the warehouse men to hold goods longer.

Food prices have been advancing rapidly and in part at least this has been attributed to the increasing practice of holding foodstuffs in storage and because of this fact, as well as because of the impression that they are of poor quality, cold-storage foods are viewed with disfavor by the consumer. This feeling, coupled with the constantly increasing tendency to throw additional safeguards around the food supply, has prompted the introduction of cold-storage bills in many of the state legislatures. In one state at least, namely Indiana, such a bill has been enacted into law. The bills up for consideration in the various states vary widely in character and on the whole show a great lack of information as to the purpose and practices of cold storage. In some measures the time limit placed upon the storage of foodstuffs is so short that the passage of such a law would demoralize the produce business and instead of reducing prices on foodstuffs would bring a return of former conditions of plenty during the season and scarcity throughout the rest of the year.

The Indiana statute is entitled "An Act for the protection of the public health and the prevention of fraud and deception by regulating cold storage and refrigerating warehouses, the holding of food products stored therein and the sale of such products." It requires that foodstuffs which are entered into cold storage shall be marked with the date of entry and that when withdrawn for sale they shall show the date of removal. All food products placed in cold storage shall be withdrawn at the end of nine months. It is provided, however, that such goods shall be subject to inspection as to their sanitary condition and that if the goods are found unfit for food they shall be destroyed. The authorities are furthermore instructed to condemn and close any warehouse which is not kept in a sanitary condition. This measure does not discriminate against cold-storage goods in favor of goods which have not been so kept, but it does provide that the purchaser of eggs, poultry or meat may know how long the goods have been in storage. Another section providing that the warehouse records shall be subject to inspection, and so making it possible to determine the amount of goods held in storage, will have a tendency to regulate the too frequent practice of speculation in the food supply.

During the past year foodstuffs, notably eggs and meat, have commanded very high prices although there was in cold storage an adequate supply of both products. The fact that the owners of much of these goods were obliged to sell at a loss and in many instances were driven into bankruptcy at the close of the season, does in no way compensate the consumer, who during most of the months of the year paid high prices for foodstuffs although following the break in prices, they for a short time were sold below their actual value.

Cold storage is necessary to the conservation of food products. It is to be hoped that the public will learn to appreciate more than now its value. It should be regulated by practical laws which do not have for their purpose the destruction of the business but which are intended rather to put a stop to the practice of storing foods which are not suitable for refrigeration but which have, even before entry into storage, deteriorated or become unfit for food, and to assure the withdrawal of all goods before they have been held sufficiently long to undergo partial spoilage. Such legislation will also be of decided benefit to the cold-storage industry as all products will be subject to inspection and to this extent at least the quality of cold-storage foods will be guaranteed to the consumer.

H. E. BARNARD.

ADDRESSES.

CHEMICAL RESEARCH AND INDUSTRIAL PROGRESS.¹

By WM. H. WALKER.

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Within the last few years research has become a word to conjure with. Webster defines it as "diligent

¹ Address of the Retiring President of the American Electrochemical Society, New York, April 7, 1911.

inquiry in seeking facts or principles, continuous search after truth." To find the truth, is, therefore the keynote of research. But although the great activity in research which so marks the present is essentially modern, an inquiry after truth is surely not new. The human mind has from the gray dawn of

antiquity longed for and sought after truth. The new field of human endeavor epitomized by the word research represents a change in the method of finding truth rather than in the intensity of desire to know the truth. When a great thinker of the past wished to investigate a subject he simply sat down in a quiet nook or walked through academic groves and philosophically meditated concerning it. He believed that he could know things as they are and had great faith in the accuracy of his conclusions. As a mental performance such philosophical labor was not altogether without value—but since we cannot know things as they are, but must know them as they appear or manifest themselves, a search for truth can reach its goal only through intimate contact with the things themselves, and an accurate determination of the facts concerning them.

At the time when the followers of Aristotle were speculating upon the constituent parts of the universe, and concluding that everything was composed of fire, water, air and earth, with the material transformations which each could undergo, there were other men who were devoting their attention to the real transformation which materials do undergo. These people had glass, a product showing a marked change when compared to the raw materials going into its production; they were able to dye the royal purples and to bleach the fine linens. They had the knowledge to smelt iron and copper, tin and lead from their ores—surely striking transformations which they could actually see. But the truth concerning these phenomena did not interest the men the achievements of whom history has seen fit to chronicle. The dictum of Aristotle that "industrial work tends to lower the standard of thought" prevailed, and it is to this want of sympathy that we must ascribe the fact that the old historians failed to note the discovery of even the most important chemical processes, while they gave detailed accounts of those men who advanced mere speculations and taught untenable opinions on the constitution of the universe.

But groping in the utter darkness of these early times, the men who actually did things in the utilization of natural phenomena in contradistinction to their more famous brethren who only talked and idly speculated about them, were the real pioneers in chemical research. Their quest for truth was however so crude, and their endeavors so little appreciated, that almost no real progress was made. The teachings of the philosophers that there was required but the "quinta essentia" in order to transform one of their four elements into another, together with accidental observations on the part of some pseudo-scientists, led to that studied attempt to transmute the baser metals into gold which lasted for many centuries. If but the "Philosopher's Stone" could be found, the problem would be solved. This was the goal of the alchemists. It would be a perversion to describe the labors of these men as a search for truth; their objective point was gold, not truth, and many a devoted life was spent in this fruitless quest.

It may seem a long step from the work of the al-

chemists with all their magic and mysticism, their sordid lives, and their cherished secrets, to the consideration of the intense human activity of the present day with those gigantic undertakings and marvelous achievements, collectively called modern industry. But there may be something in common between the work of the ancient investigators and their influence on civilization, and chemical research of to-day and industrial progress.

The course of human events has been compared to a pendulum. We tend to swing to extremes: to go too far first in one direction and then in the other, when real progress lies in the middle. The period of alchemy represents the pursuit of science for selfish and mercenary ends; they cared for nothing but to be able to make gold. The pendulum was at an extreme end of its path. Nor did they make material progress in their methods. The alchemist of Arabia and early Germany were little wiser than their predecessors of Egypt who flourished many centuries before them. The explanation of this lack of progress is to be seen in the profound secrecy which they at all times maintained. When some enterprising worthy did take it upon himself to transcribe for future generations his knowledge of the mystic art, his sentences were so ambiguous and his diction so involved as to make the whole entirely meaningless. They even employed mysterious symbols to render the more difficult any attempt at imitation.

There was therefore, no accumulation of knowledge or experience, and each succeeding investigator continued to grope around in the darkness which had ever enveloped his calling, without deriving any benefit from the labor of either his predecessors or his contemporaries. The great and insurmountable obstacle to progress was nothing more than the jealous secrecy engendered by selfish competition. Both confidence and coöperation were entirely wanting. Each one feared that his neighbor might profit by his experience were it to become known, never realizing that he must in the end get much more in return than he gave. There was but one of him, while there were many of his neighbors.

But in the thirteenth century there came a change. One Roger Bacon, who from his rare accomplishments and erudition was called Doctor Mirabilis, and who firmly believed in the existence of the philosopher's stone, was being tried at Oxford for sorcery. To disprove the charges against himself, he wrote a celebrated treatise with a long Latin name, in which he showed that phenomena, which had been attributed to supernatural agencies, were in fact due to common and natural causes. He pointed out further in his brief, a possible distinction between what he called theoretical alchemy, or work which would advance the knowledge of natural phenomena, and practical alchemy, or the striving after immediately usable information. He is to be regarded as the intellectual originator of experimental research, and be his generous treatment of the knowledge gained, gave to the science the impetus for which it had so long waited. The limitations of this paper preclude my following

in any detail the development of chemistry through the succeeding centuries, but it can be easily shown that just as knowledge was sought after for its own sake, and in proportion as there was free and honest intercourse among the investigators of the time, just so rapidly was real progress made.

With the appearance of men who took an absorbing interest in the study of natural phenomena for the purpose of gaining a deeper insight into the world around them, when investigations were undertaken from a desire to know, and to acquire knowledge which could become the property of the world at large, the pendulum began to move back.

For years the efforts of investigating minds were devoted to the explanation of the phenomena of nature; to the discovery of new laws and principles; to the accumulation and organization of facts, into what is called a "Science," to a real search for truth. This resulted in a general uplift of humanity, an advance in civilization, which cannot be described or measured in a few words. It was a time when the human mind was struggling to determine realities in the midst of tradition and superstition; to realize that nature is always complex but never mysterious; their dependence should be placed in proven facts rather than the vagaries of priests and philosophers. Man became intellectually free.

But for many years after the broad generalizations upon which modern chemistry is founded were well established, industry did not profit much by scientific work. One hundred years ago the men who smelted the iron and copper, the lead and zinc, knew little of the principles underlying their practice. Leather was tanned, woolens, cottons and silks were dyed, porcelain and glass were made, without the aid of those who alone knew the chemistry involved. I do not mean that scientific men took no interest in the manufacturing industries, for we can recall the great work of Liebig for agriculture, and the immense amount of analytical chemistry which is the foundation of industrial chemical practice; but these were times when the advance in chemical knowledge was far ahead of the industries on the success of which our material comforts depend. The pendulum had swung to the other extreme.

A rational attempt to apply chemical knowledge and methods commenced about 1850. It was in 1856 that Perkin made the first synthesis of a coal tar color, and founded the industry which has become the most remarkable example of applied chemistry that we have. In 1855 Bessemer introduced his revolutionary process for making steel, made possible by the clear understanding of the nature of steel through improved analytical processes.

Up to this time when a man became a student of chemistry, it was because of the attractions which he found in scientific study; because of his "delirious but divine desire to know." On the other hand a man who intended to devote his life to the carrying on of some industry did not study chemistry at all, or if he did, it was in a superficial and most perfunctory way. With the establishment of great technical

schools there was produced a class of men who, notwithstanding the fact that they intended to follow industrial work as a career, studied chemistry in such a way as to become masters of the fundamental principles underlying the science, as well as possessors of a great mass of scientific knowledge and experience. Possibly more important even than this, they became imbued with the scientific method of thought and work. Such men carried science into the industries and applied to the solution of the practical problems of the day the knowledge of chemistry which was theirs. Hence the last fifty years may be said to be characterized by the production of men who combined the ability to appreciate and enjoy work in science for itself alone, but also possessed the ability and inclination to apply their chemical knowledge and training, and to make the results of past generations of pure scientists of ever-increasing service to humanity.

But within the last ten or fifteen years we have seen a third kind of chemical activity develop, namely a class of men who while possessed of the ability and love of science which characterized the leaders in pure science of old, yet are not handicapped by the doctrine of Anstette, that contact with industry contaminates thought. This movement is seen in the tendency of great industrial organizations to establish research laboratories within themselves, and in the willingness of educational institutions to maintain research work in these fields of chemistry which are immediately applicable to industrial practice.

For the purpose of further studying the relationship existing between chemical research and industrial progress, we may therefore divide this kind of chemical activity into three classes: First, we have that which for want of a better term we will call original work in pure chemistry; second, we must consider the work of the so-called industrial chemist, the man who primarily applies existing chemical knowledge to the accomplishment of specific ends; and third, we have research work in what again for want of a better name, we will call applied chemistry.

It is but a truism to say that there is no more dignified honorable, or altogether delightful calling in life than the pursuit of science for her own sake. The biographies of the great altruists of science are ever an inspiration to the student of human progress. The man who devotes his life to the accumulation and dissemination of knowledge without thought of return other than the gratification incident to discovering nature's secrets, and adding to the sum of the world's knowledge, is living in many respects an ideal existence. But such men must subsist and if the results of their work bring no financial return they must have some vocation for which the world is willing to insure payment. Thus it comes about that for the most part our educational institutions have been the source from which such work has sprung. The environment of pure science has in the past been academic; its home has been in the schools of learning; the great investigators were teachers. Of course there are exceptions, but the honor roll of science is

essentially an academic list. This is true in America as in Europe, and yet there is a very different attitude shown towards men of science and their work by the manufacturing public, here and in Germany for example. There, the dictum of the university carries authority, while our feeling is shown rather clearly by our very general use of the word *academic*. It is usually a term of mild contempt, and is used synonymously with impractical, unworkable, and a lack of acquaintance with cold facts. That great scientist, Prof. Wm. Ostwald, when addressing the Liverpool Section of the Society of Chemical Industry, on the causes of the great success of the German chemical industries, said in substance: "We might sum up the facts by saying that Germany managed to put more brains into her goods, or if we prefer a more scientific expression, to combine more mental energy with the rough energies of primary material. There is no doubt that the English store of mental energy is as great as that of Germany, the only difference being that the channels leading that energy into industry were not so broad or deep or numerous as in Germany. There seems to exist in parts of Great Britain not only a disregard for, but even a mistrust in science or theory. In Germany everybody trusted science, even the Government. They were quite accustomed to consult a scientific expert before going into a new business. Of course there were cases in which they failed to act in this way, but then they generally fell into scrapes. Sometimes even theory led into scrapes, but it proved to be bad or incomplete theory. But the sum total of experience has convinced them of the value of theory, and their trust in it was rather too large than too small."

This statement does not apply alone to England. Our American industries have flourished very well, it is true, but rather in spite of a lack of scientific aid, than on account of such aid. This high regard with which science is held by even the less educated manufacturers of Germany, while undoubtedly the true basis of the splendid achievements resulting from coöperation of science and industry, is probably not to be realized in America in the immediate present. High respect for science is a characteristic of the German, and is possibly a result of years of military discipline as a part of a monarchical government. Can it be true that the spirit of freedom has run so riot in America that we now come to believe that we are not subject even to the laws of nature? Supplied with bountiful resources far beyond what any other nation enjoys, protected by a tariff wall higher and tighter than those of our commercial competitors, we have grown vastly satisfied with our own achievements. To quote from a keenly observant contemporary:¹ "We marvel at our enterprise in scraping iron ores from the earth's surface by steam shovels, in growing wheat on virgin soil, in stripping great areas of primeval forests, in burning natural gas, and allowing petroleum to spout from the ground. Even Germany acknowledges that she cannot compete with us in raising cotton, and we cut more ice in a

month in the single state of Maine than all the Pictet machines in France can turn out in a year. We control the copper market of the world because we have the copper! If cheap sulphur is wanted, we pump it from the ground! We develop great centers of power distribution, because our rivers run so fast down hill! To these vast resources we have, indeed, brought a native energy, an unusual capacity for organization, and a genius for mechanical affairs. What we do we do on a large scale, but we often do it very badly. It is quite time for us to pause in our self-congratulation long enough to inquire whether the things we are doing cannot be better done, whether in fact other nations have not developed and put to use much better methods, which, given an equal opportunity, put our performance to the blush."

There is thus a mutual obligation existing between our educational institutions and our industries. The former must continue to increase their facilities for that research, which has made the German Universities the avenues through which German civilization and industry have been brought to the point that we find them to-day.

On the other hand, the industries should not fail to recognize that progress based alone on industrial prosperity is but apparent progress, and that a sound civilization depends not only on conditions which make for material comfort, but on the culture which comes from an education, the broad sense that scientific research implies.

The great tendency of our times is towards service. This is seen in every sphere of human activity. The philosophy of even one hundred years ago was largely speculative; while doubtless mentally invigorating, it did not in the last analysis contribute toward that progress which alone makes life worth the living. As a result, all past systems of philosophy have been thrown back into the realm of literature or of poetry. The trend of modern philosophy is toward a study and realization of things as they manifest themselves, and not a mere guess at what things probably are.

In religion too we note a change. There was a time when the main object of one's religion was to save one's own soul, without much regard to the souls of others. But we no longer recognize particular virtue in shutting one's self up within heavy walls, in order to render one's life more pure, because of lack of contact with the great mass of humanity. We no longer admire the self-sacrifice of the immured monks of Thibet—we simply pity them. Religion is to-day the great inner consciousness, which renders one's own future condition secure by aiding the present condition of others. The great religions of to-day make for righteousness through service.

In the same way there is with scientific men a general awakening to the fact that the highest destiny of science is not to accumulate the truths of nature in a form that no one but the elect few can utilize, but that the search for truth can be combined with a judicious attempt to make the truth serve the public good. Thus the distinction which has existed between the terms pure science and applied science is rapidly

¹ Arthur D. Little, in "A Laboratory for Public Service."

falling away. An attempt to define these two kinds of science reveals the fact that their distinction is a general impression rather than a clear statement. A fundamental law of psychology is that thought tends to pass over into action. Applied science is nothing more than the realization of this, and is thought in action. Force does work only when in motion—so are ideas of value, only when carried into effect.

But the carrying of an idea into practice is not always an easy matter. It is frequently much easier to make a discovery or to develop a new fact than it is to make of such a discovery a serviceable reality. For example, the reactions underlying the ammonia-soda process were well-known as scientific facts for many years; but this knowledge did not benefit the world until the genius of Solvay made through it purer and cheaper soda available. Cavendish long ago discovered that an electric spark produced nitric acid in the air; the world waited until but a few years ago in order to profit by this knowledge. It was then that the researches of Birkeland and Eyde made of the idea an industrial process.

Many facts like this last were known which did not materially influence the industries of the times because there was necessary a knowledge of how to obtain and apply large quantities of electrical energy. Thus Wohler discovered the reaction by which phosphorus could be readily distilled from a mixture of bone ash, sand and coke; but it remains for Readman and Parker to apply internal heating by electrical means to thus make phosphorus. Wohler also discovered calcium carbide and its property of yielding acetylene. The beautiful light from this source was not made possible, however, until the development of high-powered electric generators made its cheap production an easy matter. Men who can interpret the scientific results already available have been of incalculable value in the growth of our industries, and there will ever be a field for this type of chemical activity. In fact it is just here that we find the faith in science of the Germans of which I have spoken bearing fruit. In America there is a national lag in the application of new scientific data to every-day problems. We as a people are so wonderfully keen in developing mechanical ideas when once they are presented that the marked lag in the acceptance and application of chemical principles is remarkable. The industries themselves are frequently to blame for disappointing results which sometimes are met in an attempt to introduce scientific methods into their works. They employ a so-called chemist, without inquiry as to whether he has had the kind of training that could be expected to fit him for the work he is to do. They furnish him with a meagre equipment and then expect revolutionary results. When these are not forthcoming they exclaim in disgust: "There is no money in chemical control, or in chemical research—we have tried it." It is just as though I should decide to increase my income by adding to my other activities that of horse-racing. I buy a well-meaning, but untrained horse, and enter him for the race. He fails

to win the purse, and I exclaim: "There is no money in horse-racing, I've tried it." Or probably my analogy would be more complete if I would suppose that I bought a well trained, capable horse, and then hitched him to a coal wagon or an ice cart, and started him off. Then because he fails to win out over the horses in racing sulkies, I again affirm: "No, there is no money in horse-racing, I've tried it."

While it is true that the manufacturing industries as a whole have been slow in accepting the aid of science, and while the American public lack the belief in the part which science plays in the advance of the world possessed by some other nations, there is a distinct and most promising movement under way, which will have a marked effect upon our industrial progress. This is the impatience shown by some of the more enterprising manufacturing concerns, to wait for scientific facts to be discovered by others, and their willingness to establish research laboratories within their own organizations; to actively enter the field of research in applied chemistry.

From what has already been said, there may appear to be a paradox in the expression research in applied chemistry. How can the element of research enter into the work of applying to definite ends the facts already established as true by others? Is there a difference between research in so-called pure chemistry, and research in what, for want of a better name, we will call applied chemistry? Possibly I can make the distinction clear by a rough analogy. The development of research in a science may be compared to the exploration of a new country. New roads are to be laid out, tunnels bored, and bridges built; in other words new problems solved. This may be done in two ways. First, constructive work may be undertaken wherever an interesting problem presents itself, without regard as to whether there is a demand for such structure, or not. It is built because of the interest of the builder in solving this particular difficulty, and the pleasure he takes in it, knowing also that sometime it will be utilized. As a rule he is under no great pressure to get the structure completed. This may represent the method of pure chemistry, and the great advance in chemical knowledge of the past was made almost entirely by boring just such tunnels, and building just such bridges. The industries have used these structures when they could, or when some second builder could adapt them to use. Research in applied chemistry differs from that just described only in this—I should say it *needs* differ only in this, that when a problem is to be solved, a bridge to be built, the work is undertaken at a point where there is a demand for its use; where people are waiting to cross over, so soon as it is finished. The method of building is no different, the difficulties no less. The fact that the bridge is to be used, makes the work of building no less dignified, nor is it possessed of less pleasure. In both cases the builder profits by all that has been done before, and contributes his bridge together with the new materials of construction which he may have found, to those who may come after him. To cite an example from experience, sup-

pose I were to determine the electrical conductivity of metallic oxides at high temperature, with great accuracy, and publish the results without reference to any particular application of the data. This is pure science. But suppose I am trying to perfect an electrical heating unit for high temperatures, and in insulating my resistor, I do this identical piece of work, namely, measure with great accuracy the electrical conductivity of metallic oxides at high temperatures, and again publish the results. This is applied chemistry. The work need not differ in the least degree. It can be as accurately done, and the conclusions as scientifically drawn. The mere fact that the data will be used for some practical end, need not make the investigation any less scientific.

Why is there then not the respect for this kind of work, as when a bridge is built with the knowledge that it may not be used for an indefinite period? Why then does an eminent writer a few months ago lament the fact that there is not more research "uncontaminated with the worship of usefulness?" Why does usefulness contaminate? I think it lies in this: the investigator of pure science works in the broad daylight; throws his product open for inspection, and invites all to come and use it when they can. In applied chemical research the spirit of the alchemist tends to creep in. The builder keeps his materials of construction, and his designs, a secret, and so boards up his bridge that those who cross over it cannot see how it was built, nor profit by his experience. The moment a thing becomes useful we become jealous of its possession; we become narrow in our horizon; we sell our scientific birthright for a mess of pottage; we become alchemists.

There is a heavy moral obligation on the part of large industrial organizations having fully equipped research laboratories, to contribute their share to the advance of the world's knowledge. An obligation to see to it that they do not become saturated with the spirit of alchemy. They have well stocked libraries, and are provided with all the current periodicals; they profit by all the scientific work which has been done and is being done. This is as it should be, and such firms are to be commended for their progressiveness. But is this not a reason why such laboratories should do their part in adding to the sum of available knowledge? There is in every laboratory much work which could be published and yet conserve the interests of the corporation. First there are the results which may not have proved valuable to the laboratory in which they were obtained, but which would be of immense value to some one else working in an entirely different field. Second, there are those results of value to the laboratory possessing them, but which could be published in an unapplied or "pure" form and which would make an important contribution to science, and at the same time the publication would work no injury to the company or the corporation most interested. And finally there are those results of operations and processes, machines and apparatus, which if the truth were known are possessed by a number of concerns, but are held as valuable secrets by each.

Every one would profit and no one be the loser by so far-sighted and generous a policy. Germany is very justly held up as a shining example of marvelous industrial progress and prosperity. A very great deal of the credit for her present position is due to her splendid educational system. But no small factor in her national progress is the helpful attitude which her industrial organizations take toward the publicity of scientific data. The individual does not suffer, while Germany both from a purely scientific and an industrial standpoint is rapidly advanced. But too often with us the President and his Board of Directors are alchemists; they fail to see why if they pay the salaries of the research men, they should give to the public, or their competitors, any part of their results. They exclaim: "What has posterity done for us?" They would have their laboratories remain the secret chambers of the alchemists, and continue to improve their methods of changing baser materials into gold, without regard to the obligations which they owe their fellows.

It is to the men who form the working force in our industrial laboratories that we must in a great measure look for making our national scientific societies the power for industrial progress which they ought to be. But it is this general disinclination on the part of industrial concerns to allow their chemists to disclose in any measure the results of their work by contributing papers for the meetings, or in entering heartily into the discussions that make this realization difficult. This is to be deeply lamented, and we believe it is a fundamental mistake: a short-sighted policy which can but react upon industrial progress as a whole. We cannot operate a scientific laboratory as we would do a factory. The conditions of maximum productiveness are not found in an atmosphere of selfish rivalry. An English writer of broad technical experience has said when speaking of the cry for technical education: "Until the nation, as a whole, recognizes that the prosecution of scientific study as a mere means of money-making is a profanation defeating its own ends, the history of the industrial development of England will afford the same melancholy spectacle in this as in the last century, technical education notwithstanding." All attempts at machine-made scientific results are doomed in the long run to failure. They compare with the achievements of men working under conditions of mutual helpfulness as does a machine-made Nottingham curtain compare to the beautiful hand-made lace of the French convents.

It requires no extensive mathematical calculation to prove that the manufacturers themselves would be the ones to profit by such a liberal treatment of the results of scientific work. Of one hundred manufacturing concerns, each one would give but 1 per cent. of the whole contribution, while he would receive the remaining 99 per cent. He could not in the long run be the loser. But of vastly more importance, he would feel and know that his organization was taking part in a world movement toward that increase of human knowledge upon which all real progress depends. The greater sense of satisfaction, the greater

success even of an industrial organization, lies in a fuller, freer, more generous publicity of the scientific results of their laboratories.¹

Would that we might benefit by the experience of Solomon, King of Israel, who, when asked "What shall I give unto thee," replied, "Give me knowledge and wisdom," and he was answered, "Wisdom and knowledge are granted unto thee; and I will give thee riches and wealth and honor."

CONTRIBUTION OF CHEMISTRY TO SANITATION.²

By WILLIAM P. MASON.

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It must be noted at the outset that the above title is confessedly too broad for a single paper, so that only a small part of the large field can be here touched upon, leaving the balance to be covered by others better qualified to deal with its several portions.

Within the memory of most of those present the public took but a slight degree of interest in the hygienic character of drinking water, and while they evinced some concern as to the analyses of supplies for boiler or for laundry purposes, the water intended for table use was judged as to its fitness by its physical properties alone.

Although it is still hard to convince some people that anything can be wrong with a water which is acceptable to the senses, yet the wave of education in such matters has extended far and we find a material amount of inquiry as to the nature of a supply which is offered for public consumption.

No one familiar with the way the laity view things chemically needs to be reminded of the existence of a firm belief wide-spread among them that laboratory results alone are quite sufficient foundation whereon to base an opinion concerning the suitability of a water for household purposes. No chemist has to be told of the fallacy of such a notion, but for the benefit of such of the non-professional public as may be here present, let it be said that of the three forms of water examination, "chemical," "bacteriological" and "inspection of the source," the third is altogether the most important. While none of these procedures should be wanting for the formation of a safe opinion as to purity, yet though it may sound like heresy to this audience it must be admitted that either of the two laboratory methods taken alone is, in general, inferior in value to a careful "sanitary survey" conducted by one trained in such work.

It was said above that within our memories but little interest was shown in the chemical analysis of table waters. As a matter of fact, there was but little in the analysis itself wherein interest could lodge. I very well remember the occasion of my first analysis of that kind. The method of attacking the problem was simplicity itself: Evaporate to dryness for total solids; ignite to redness; restore lost carbon dioxide by use of ammonium carbonate; gently ignite off excess of the said salt; weigh the inorganic solids, and

the work was done. Of course bacteriology was not yet born, or rather it was still in its infancy. Fancy the kind of results that could be secured by a method such as the above when comparing a harmless moorland water, high in color, with one drawn from a typhoid infected well. The heavy "char" would arouse suspicion in the first instance, and its absence would "pass" the second sample as pure.

Following quickly upon such crude procedures came the complete combustion process of Frankland and the albuminoid ammonia method of Wanklyn: the former destined to make but small headway among analysts in this country, and the latter, though modified, to be widely adopted. Bacteriology, although still in the background, was making rapid progress and a little later when it did come to the front, it forged ahead of its legitimate position, as did radium, and tuberculin, and 606 and other examples of over exploited discoveries. Those were the days when pronouncements were confidently uttered as to the presence or absence of the *bacillus typhosus* in any water sample submitted for examination: the days when chemistry was expected by some to shortly retire from the sanitary field so far as water work was concerned and when chemists and bacteriologists held very different and very hostile camps when considering the "water" question. It does not seem so very long ago that the writer was invited to attend a meeting in New York of chemists and bacteriologists, the topic of the hour having been which method of examination gave the more correct decision as to the safety of a water for domestic use. Is it to be wondered at that when the question was finally called for the votes grouped themselves in entire accordance with a prophetic utterance delivered before the meeting began.

We have outgrown such discussions now, knowing as we do that neither bacteriology nor chemistry can by itself answer all the questions that may arise, and to-day the water examiner is only too glad to call to his aid the contributions offered by both sciences.

Since the radical changes in methods of analysis inaugurated by Frankland and Wanklyn were first presented the alterations in chemical procedure have been rather of the nature of modifications than the introduction of new processes, or at least that is true for what may be termed "routine" water analysis.

Sundry of these modifications have been very acceptable, such as the statement of "turbidity" and of "color" in "parts per million" rather than in descriptive words as of old, and also such as the quick methods for detection and determination of the metals. Weston's method for manganese is an instance in point, and the use of "formaloxime" to detect copper in solution is another. The latter is especially useful since the employment of copper sulphate for destruction of algal growths has become so frequent.

The examination of water for the presence of the heavy metals is certainly more often undertaken than it used to be, and there is a growing feeling that it is wise to go beyond a simple statement of what metal is actually present in the sample at the time of analysis

¹ Dr. Carl Otto Weber in *The Chemistry of India Rubber*.

² Paper read at the dedication of the Chemists' Club, March 17, 1911.

and to determine what the water in question would do in the way of acting upon the common metals should it come in contact with them. In other words there often is great value lying in a foreknowledge of just what may be expected should some certain water be sent through pipe of specific character. For that reason it is the part of wisdom to experimentally test the action of a water upon sundry metals and to state the result as a note to the analytical report.

Although we know in a general way that softness, acidity, dissolved gases and the presence of much chloride or nitrate will tend towards metallic action, while alkalinity and hardness are rated as protective agents, yet it is far better to actually test a water with reference to its behavior towards metals than to attempt any prophecy of what it will do based upon analytical knowledge of its contents. And we may add that the rate of action of the same water is not only variable, but the ratio of the total action during different lengths of time is not a simple one. Thus, the quantity of metal attacked in ten hours is by no means ten times that acted upon during one hour.

In one particular chemistry has shed no recent light upon the subject of water analysis and that is in the matter of testing for "chlorine." Knowing as we do that chlorine forms a part of every pollution from sewage inflow it would aid us greatly did we have a reliable means of detecting small variations in the quantity of it present. When we recall the great delicacy of some of the other tests in a routine water analysis we are struck by the comparative crudeness of what is available for chlorine. If some really delicate test for it were at hand then closer estimation of the amount of "cyclic salt" could be had, better maps of "normal chlorine" would result and a needed revision of the per capita influence of population upon a water-shed would follow.

"Hardness" determination is another item with which the water analyst is not entirely satisfied, but the necessity for close accuracy is not so important in this case, as is shown when we consider the difficulty of interpretation. The question "What is a hard water?" is not an easy one to answer. Of course waters lying near the extremes of "hardness" and "softness" may be readily classified, but there is a pretty broad middle zone where doubt begins to appear and one is forced to conclude that personal likes and dislikes enter very largely into the question.

After looking into the hardness of many waters on the Atlantic coast, the writer finds that the users of those waters are possessed of great variety of opinion touching the merits of their several supplies: for instance, a hardness of 41.0 parts per million is rated as "a little hard but good for washing;" a hardness of 31.0 as "good for boilers but not entirely satisfactory for washing;" a hardness of 46.0 as "very good;" another hardness of 46.0 as "not satisfactory;" a hardness of 63.0 as "too hard for boilers or laundry;" and a hardness of 70.0 as "complaint from laundries only."

From a consideration of expressions of opinion such as quoted, the reasonable division would seem to be to

class as "soft" all waters below 50 in hardness, to call "hard" those that run as high as 100 or more, and to leave the space between these numbers as a kind of debatable ground wherein individual views shall govern.

As with "hardness" so with "iron," so far as popular opinion is concerned. There are many contradictory statements regarding the amount allowable in public water; thus among the eastern waters above cited as much as 0.72 Fe per million was allowed to be acceptable, while in another city complaint was entered against 0.38.

The layman knows from his own experience whether or not a water is producing scale in his boilers or is making red spots on the linen in his laundry, so that the chemical analysis merely furnishes reasons for a knowledge of the facts already in his possession; but he does not know if drainage be entering his drinking water, nor can he find out by inspecting the analytical data. To him the figures on the report sheet are meaningless and he demands an interpretation of them. Such an interpretation the chemist cannot always correctly give, using his data alone, for he needs the aid of the bacteriologist to supplement his own work and yet he sometimes does by himself what the bacteriologist can never do, namely, foretell future danger in a water which for the time being is not harmful. No better illustration can be given of the dependence of these two branches of science one upon another than the instance of that well water which, though harmless at times, became dangerous during periods of wet weather. Chlorine from the contents of a neighboring cesspool was always present in the water of the well, but, except when overtaxed during stormy weather, the intervening soil presented an efficient filter against the entrance of intestinal organisms. Thus chemistry at all times hung out the warning flag while the sister science was powerless, except at intervals, to show the danger.

Of course illustrations of a reverse condition of affairs can be cited. Take for example a very recent case. Badly polluted water was passing into a city's conduit line through a leaky "emergency" gate, and chemistry, because of the great dilution, failed to detect this fact; while on the other hand the character of the bacterial contents of the water immediately aroused inquiry and the trouble was located. Many similar citations could be given.

Before leaving the topic of interpretation of analyses it is right to add that we cannot but deplore the fact that not a few opinions are still given without sufficient knowledge of the conditions surrounding the source of supply; that is, without "the sanitary survey." Not long since the writer had to do with a deep water of most excellent character which a town in the west had been fortunate to strike by rock boring. A sample of that water was shipped a long distance and examined by a man who condemned it upon laboratory information alone, to the very great disadvantage of the people interested. High nitrates and nitrites, or none of these and high ammonia, may readily be found in deep waters; high chlorine

is common enough and of course a high count of bacteria must be expected from samples not packed in ice during transportation. Is not the risk of venturing an opinion on laboratory data alone pretty much the same as that assumed by the physician who formulates a diagnosis and writes a prescription without seeing the patient?

Finally, let it be said that a water analysis is, for purposes of economy, rarely made complete. For ordinary drinking water the question is always asked "is it wholesome?" To answer this, the analysis of the mineral residue left upon evaporation is not usually required, so that much time and expense may be saved by simply reporting this as "total solids." On the other hand, analysis of mineral waters deal with this feature of the examination very largely, and usually to the exclusion of those portions, such as "albuminoid ammonia," "required oxygen," etc., which are important in the "sanitary analysis." The same may be said of the analysis of waters for boiler use.

When we come to protective measures for the general improvement of public waters, chemistry is now doing much more than simply furnishing the clarifying dose of alum: a means of improvement known to the ancient Egyptians. Copper sulphate, ozone, bleaching powder and the other hypochlorites are among the resources to which the water purveyor may turn for relief in the event of difficulty.

At the time copper sulphate was first proposed as a chemical cure for stopping the plague of taste-producing algae, comment was made regarding the remark of a veteran water engineer who once said: "No one who can row a boat should fear trouble from algae." What the old man meant we now can only guess, but it may have been that he possessed the secret of "coppering" reservoirs and carried his information with him to the grave. How useful copper sulphate is in curing objectionable plankton tastes is now widely known, nor is the "coppering" of water restricted to the killing of algae alone. The process is in use for the destruction of bacteria during times of epidemic disease, although, in the opinion of the writer, ordinary bleaching powder is a much more certain agent for such work. Within a few weeks past some 19 pounds of copper sulphate per million gallons of water have been added to the supply of a western city during an outbreak of typhoid and the results have not been as beneficial as expected. Without doubt less than half that dose of ordinary "bleach" would have proved much more satisfactory.

Since the introduction of "bleaching powder" three years ago for the purpose of ridding water of pathogenic organisms the method has grown so in popularity that to-day it is not too much to say that practically all the new filter plants in course of erection have added to them devices for the introduction of "bleach," should occasion suddenly demand its use. What this chemical will do in the way of killing intestinal organisms is now a matter of common knowledge and it would seem to be an unwarranted assumption of risk to fail to provide means for quickly

supplying it in event of necessity. In this connection it should be said that "bleach" is especially serviceable under those unfortunate conditions when, because of some accident, the regular water service is cut off and temporary recourse is had to an inferior supply for the purposes of providing fire protection.

"Emergency" intakes are always sources of danger and many a life has been sacrificed through filling the mains with dilute sewage to guard against fire losses, as is instanced in the typhoid outbreaks of Butler, Lowell, Toronto and many another town. Judicious use of the hypochlorites during these "emergency" periods will remove threatened danger and is infinitely better than trusting to a notice to "boil the water"—advice which the careless portion of the community will never follow.

It is true that sodium hypochlorite, prepared by electrifying a common salt solution, may be used in place of the better known "bleaching powder," but it requires much more careful attention for its administration and it probably cannot be furnished at so small a cost. As a germicide it has no advantage over the "bleach," but it is distinctly more in favor with the general public because of its being a product of water, sea-salt and electricity, a combination which is looked upon by the people as being free from the dreaded "chemicals."

Ozone is another product for water purification which, on purely aesthetic grounds, is very acceptable to the masses, inasmuch as it is in their minds simply "electrified air." It is efficient and will do all that is claimed for it, but can we afford its use? The weak points connected with the use of ozone are: first, its cost; second, the liability of the apparatus to get out of order. These objections will doubtless be overcome in time and are reported by those interested as being already overcome. But we lack a collection of data upon a large scale. What we need is a municipality willing to take the risk of erecting a large plant operated upon the ozone system. We should all be delighted to study the results, and we should be glad to congratulate such a city in the event of success and to use the information accumulated; but would we be entirely disposed to share the expenses in the event of failure? On the whole, while we admit the efficiency of ozone and while we look hopefully towards its practical success in the future, we cannot but feel that at the present moment with the meagre data we now possess we should run considerable risk in recommending its introduction as a means of purifying a municipal water supply.

Much as chemistry has had to do with the sundry processes of water "softening," yet from a sanitary standpoint such procedures are of minor importance because the reduction of hardness is primarily undertaken for industrial reasons rather than for the protection of health.

When we consider that as Whipple has shown, "for every increase of one part per million of hardness the cost of soap increased about ten dollars per million gallons of water completely softened" and that an additional drain on the people's purse must come

from the disadvantage of using hard water for boilers and other industrial purposes, and further, when we note the inclination of sanitarians to put reliance upon the claim of English authorities that the drinking of hard water is not closely related to disease production, it is easy to be seen that long before the health authorities can cry out against the hardness of a proposed public supply there will be bitter complaint lodged by the manufacturing portion of the community.

As has been already intimated, it is exceedingly difficult for the chemist to stand alone when considering sanitary problems. His field of inquiry continually overlaps those of other scientific men and he requires their assistance to complete his work. This is especially true in water investigations, wherein, as has been said, bacteriology becomes so vitally important on both the qualitative and quantitative sides. When a water expert undertakes the solution of some important water problem he has only begun his task when he has secured a chemical analysis of the supply in question. He must of necessity supplement this with a bacteriological examination and it may be he will also have to call microscopy to his aid in order to settle questions touching the presence of local plankton involving a study of the production of taste and smell.

Of course such matters as the building of reservoirs, conduit lines and similar structures are relegated at once to the civil engineer, but some small knowledge of the fundamental principles of hydraulics must be comprised in the mental equipment of the water specialist in order that he may properly deal with the occasional questions which legitimately fall to him for answer. For instance, within six weeks past, while investigating a serious typhoid epidemic, the writer had occasion to call the attention of the city commissioners to the certainty of foul water reaching the general supply, should a leak occur in the conduit line laid on the bottom of a sewage-polluted bay. The commissioners were confident that no inflow could take place in the event of a leak because of their supposition that the water in the conduit was under pressure, a view which was manifestly in error, for there was no more possibility of internal pressure than there is in the case of a slightly inclined leader taking water from a roof. It would have been unfortunate to have interrupted the investigation until an engineer's opinion could have been secured upon so simple a matter.

It is not expected that the water specialist shall draw so largely from the science of medicine as to be able to sit by the bedside and treat a case of typhoid fever, but it is essential that he know something of the longevity of the typhoid organism, be acquainted with the conditions under which it is likely to give trouble and be prepared to rectify them. He touches the outer boundaries of those fields of science with which his daily work brings him in contact, but he does not presume to seriously enter them and when he needs information as to what they contain he applies for aid to those who know.

Allow me to quote from an editorial in a recent

number of *The Engineering News*, dealing with the proposed law for licensing engineers:

"The State proposes to grant a license to a man to practice civil engineering and to declare under the official seal of the State that the man is 'properly qualified to practice civil engineering,' which the law defines to be any branch of the profession of engineering other than military! There is about as much sense in such a proposition as there would be in declaring under the State's official seal that a man was properly qualified to keep a hotel, run a steam shovel, act as cashier of a bank, fill teeth in a dentist's office and practice law.

"No reputable and honest engineer, no matter how eminent in the profession, would dream of claiming himself competent and qualified to practice in all branches of the engineering profession."

The engineer's profession is large and varied. So is chemistry and so is sanitary science. No man can begin to cover the modern field in any one of these callings and when in the practice of his profession he finds, as he is sure to do, the more or less frequent interjection of questions foreign to his specialty, the only relief possible for him is to seek aid from those of his fellow scientists who have had experience in such problems as the one at hand. There is an interdependence of specialists which is constantly growing more pronounced in view of the ever-widening field of knowledge, and a part of the equipment of a successful man lies in his knowing just where to secure the kind of aid he needs, where to find the right man to join him in the work of a commission, where to get, first hand, that collateral accurate information which it would be so tedious and difficult for him to obtain for himself.

In view of the existence of what was above termed the "interdependence of specialists" is it not patent that a sort of chemical clearing house is needed and that a club like this supplies the want? Here men of many forms of professional activity are at home and here they may exchange their views with mutual benefit; not always in the form of critical reviews of formal papers, but often in that more valuable type of discussion, namely the intimate and friendly chat upon topics of common interest.

One of the greatest contributions that chemistry has made, not only to sanitary science, but to all branches of the broad chemical field, is epitomized in the erection of this beautiful and most useful building as the central home for the chemists of America.

COMMERCIAL PRODUCTION OF AMMONIA.¹

By C. G. TUFTS.

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The commercial production of ammonia is a fairly comprehensive subject. Ammonia has been sought in almost every nitrogenous substance and the literature of the industry shows hundreds of patents for getting ammonia from its native deposits in Tuscany and South America and for recovering it from sewage,

¹ Read before the Syracuse Section of the American Chemical Society, Dec. 9, 1910.

bones, leather and animal refuse of all kinds, and from molasses fermentation residues, from peat and from the air. Many of these sources have, at times, contributed to the world's ammonia supply, but at present it is enough to consider recovery from the coal formations and production by one or two synthetic processes. For getting ammonia from the coal formations there are five methods which are commercially important. The three best known are, of course, the gas retort, the by-product coke oven, and the Mond type of gas producer. A fourth source is the shale oil industry, and a fifth is the gas from certain Scotch and English blast furnaces in which a peculiar local coal is used.

By these methods, the world now secures about 1,000,000 tons yearly of ammonia measured as sulphate.¹ Great Britain, Germany and the United States are the leading producers, together accounting for about 80 per cent. of the total. The methods used in these countries vary, however, the gas retort being the chief source in England, while Germany and the United States rely mainly on the by-product coke oven. Taken roughly, about 55 per cent. of the world's ammonia now comes from the by-product coke oven and 30 per cent. from the gas retort, all other methods making up the remaining 15 per cent.

Taking up the various methods in inverse order of their importance from an ammonia standpoint, we should consider first the blast furnaces. In certain parts of England and Scotland there is mined a coal of such peculiarly hard structure that it can be used in the furnaces without any preliminary coking. In such cases, the furnace gases contain, therefore, the ammonia from this coal, and they are accordingly cooled and washed in water. The volume of the gases is so large, however, that cooling and washing them in water is rather difficult and at times an acid washing is used instead. In either case the resulting liquor is worked up in the same manner as in the ordinary gas plant. This method of getting ammonia will always be very much localized, but it does turn out about one-fifth as much ammonia as is produced by all methods in the United States.

The ammonia output of the blast furnaces is considerably exceeded in the distillation of the bituminous shales. At present these shales are mined chiefly in Scotland, although there are some shale operations in Australasia and also in France. The shales are roughly crushed and are then distilled in a current of steam. The distillation apparatus varies, but a standard form is a tall, vertical retort holding from one to two tons of shale and consisting of an upper cast iron section and a lower fire-brick section. The shale is charged continuously at the top and it takes about 24 hours to work down to the bottom. The upper cast iron section is surrounded by flues in which producer gas is burned, so that most of the oil is expelled by the time this section is passed. A

jet of steam is introduced near the bottom of the lower section, and the steam acting on the further heated shale expels a considerable part of the nitrogen as ammonia. The gases from the top of the retort are cooled and washed in the same manner as in the gas works. The primary object of this distillation is the recovery of the shale oil, of which the yield varies all the way from 18 to 40 gallons per ton, and in some special cases to even a good deal more. Ammonia is an important by-product, however, as the yield averages about 40 pounds as sulphate per ton of shale, and the shale works of Scotland turn out every year more than half as much ammonia as the entire product of our own country.

The next method is the Mond type of producer, and this has been put ahead of the shale industry, not because its present production is greater, but because there is more probability of growth. In the ordinary gas producer, as in the manufacture of water gas, the temperature is so high that ammonia is either not formed or is at once destroyed. In the Mond producer, however, the temperature is kept low by carefully regulating the air supply and mixing with the air a large excess of steam. Combustion thus proceeds at a temperature which never gets above a dull red and under these conditions a yield of 80 pounds of ammonia as sulphate per ton of coal is not infrequent. The gases containing this ammonia form a considerable volume and the ammonia is usually obtained by scrubbing with dilute acid.

So far, the Mond process has been successfully applied only to fairly large scale operations, and there are certain mechanical problems which must be handled carefully in order to maintain an economical operation. The large yield of ammonia, however, and the rapidly growing use of gas engines, for which Mond gas is particularly well suited, makes it very probable that this process will turn out an increasing quantity of the world's ammonia, especially since the method is also applicable to the recovery of ammonia from peat and other low-grade fuels.

The fourth method is coal distillation in the gas retort, with which operation you are all familiar. This method was for a long time the world's chief source of ammonia, and it is still of great importance. As a leading factor in the trade, however, its reign is unquestionably over. This relative decline of the gas retort output is not due to any actual decrease in the ammonia production so secured but rather to the rapidly growing use of the by-product oven in the metallurgical coke industry. During the last six or eight years this oven has so extensively replaced the wasteful beehive type that its ammonia output has far outstripped that of the gas retort.

Even in the gas industry, the by-product coke oven is being viewed more and more favorably as a substitute for the older gas retort. There are two reasons why this is so: First, a greater economy in operation. The ordinary gas retort holds about a quarter of a ton of coal, while some of the coke ovens now operating in this country take as much

¹ Recent data regarding the production of ammonia has been published by C. G. Atwater (*Mineral Industry*, 17, 26-32), by O. Rau (address to the 5th Int. Cong. of Min. and Metal., June, 1910, abstracted in *Metal. & Chem. Eng.*, 8, 478 (1910), and in *J. Soc. Chem. Ind.*, 29, 868) and in the 46th Report of the Chief Inspector of Alkali Works (1910, 19, 135, et al.).

as 14 tons of coal at a charge or 56 times as much as the gas retort. You will readily see the advantage in operating costs which is given by the use of the larger unit. A second reason is the better quality of coke. The coke from the gas retort can be used only for domestic purposes. The by-product oven, on the other hand, produces a coke which not only forms an excellent domestic fuel but is also highly prized in the foundry trade. The result is that the natural growth of the gas industry is being met to a greater and greater extent by the installation of by-product coke ovens. In the United States, cities with a total population of over 5,000,000 now get part or all of their gas from coke oven plants, and the output of gas for this purpose amounts to over 35,000,000 feet daily.

All of these factors have combined to give the by-product coke oven its present preponderance in the ammonia industry. In Germany, only 12 per cent. of the total ammonia now comes from the gas retort. In England, the gas retort still holds supremacy, but it is by a very narrow margin. The ammonia output of the English gas retorts has increased only 10 per cent. in the last six years and for the last three years has been stationary, while the output of the coke ovens has in six years increased over fourfold.

In the last few years there have been introduced in the gas industry various modifications, such as inclined retorts, vertical retorts, and the continuous carbonizer. These modifications, especially the last two, show an improvement over the older horizontal retort and for some time to come will undoubtedly find a place in the towns and smaller cities. They are, however, only the product of a period of transition in which some form of by-product oven seems to be the logical goal.

We come now, therefore, to the by-product coke oven, which in a relatively short life has jumped to front rank in the ammonia industry. It is of interest and some gratification to us in Syracuse to remember that our city was the first in America to recognize the value of this oven. The first ovens built in America were erected at the works of The Solvay Process Co., in 1893, and this seed has spread until 75 per cent. of the country's ammonia is now produced in this manner.

The by-product coke oven, as most of you know, is a long, narrow chamber usually horizontal but sometimes inclined. The capacity varies in different plants from 4 to 14 tons of coal at a charge, and the chamber is heated by gas burned in horizontal or vertical flues in the side walls. As with the gas retort, the yield of ammonia from the by-product oven is only about one-fifth of what could be expected if all the nitrogen in the coal should be converted. Attempts have been made to secure a larger proportion of the nitrogen in the form of ammonia, but these attempts have all developed some objectionable feature and there is no method to-day which will recover even half the nitrogen and at the same time produce a prime metallurgical coke. Distillation of the coal is more complete in the coke oven, however,

than it usually is in the retort. In addition, the by-product coke oven lends itself particularly well to a close and careful regulation of the coking process, a matter which is as important in getting a high quality of coke as in getting good by-product yields.

In order to recover the ammonia from the coke oven gases, the gas is usually cooled and scrubbed with water in some one of several standard ways and the result is a brownish, or yellowish, liquor carrying from $1\frac{1}{2}$ to $1\frac{1}{2}$ per cent. NH_3 . This liquor is distilled with lime in a column still and the concentrated NH_3 vapors are either absorbed in acid, or condensed to form the so-called crude liquor, or passed through purification apparatus which is more or less extensive according to the product desired and are then absorbed in water as a refined ammonia liquor.

In the last two years this procedure has at times been modified by the use of the "direct" sulphate process, which aims to pass the oven gases directly through the acid, thus getting ammonium sulphate at once and doing away with the ammonia concentrating apparatus and saving the steam and water required to run it. To make a clean, salable sulphate in this way, however, it is first necessary to get all the tar particles out of the gas, as otherwise these would discolor the salt. At the present time there are three methods in use for accomplishing this. In one of these methods the tar is removed by cooling the gas just as in the older practice and the gas is then reheated and sent into the acid bath hot. While this removes the bulk of the tar it is still necessary to retain all the apparatus for cooling the gas and it is also necessary to keep the ammonia concentrator. This is because the cooling of the gas condenses a lot of ammonia liquor as well as the tar, and the liquor must be distilled. This process, therefore, saves only a part of the steam and water used in the older methods of recovery, and it does away with only a portion of the apparatus. A second process goes further, since it entirely avoids both the ammonia still and the gas-cooling equipment. In this process a jet of tar is sprayed into the gas and the gas is then passed through an apparatus containing baffle plates. The larger drops of tar are caught on the baffles and carry down the small drops and the tar fog with them. This process is the simplest of all direct sulphate processes, but you will readily see that it is at times hard to get a sufficiently positive action from simply spraying tar into the gas in this way and there is danger that the salt made would be liable to occasional discoloration with tar. The third process goes even further, therefore, and actually washes the tar out of the gas by bubbling the hot gas through a body of tar held at temperatures which are very carefully controlled. This process takes a little more apparatus than when the tar jet is used, but it has the advantage of removing the tar in a thorough and positive manner, permitting the continuous production of a clean and high-grade sulphate.

In addition to the direct sulphate process there is another system of getting ammonia from the oven

gas which is interesting from a technical standpoint, though it has not as yet been widely applied. This aims to utilize the sulphuretted hydrogen in the gas and so avoid the purchase of sulphuric acid. The oven gases are accordingly cooled and freed from tar and are then scrubbed with either FeSO_4 or with ZnSO_4 . In either case $(\text{NH}_4)_2\text{SO}_4$ is formed and the metals are precipitated as their respective sulphides. These are filtered out and regenerated and the $(\text{NH}_4)_2\text{SO}_4$ is secured by boiling down the filtered solution. A modification of this system is a process in which the unscrubbed oven gas is passed over a specially prepared iron hydrate. The sulphides of iron formed are burned, regenerating the hydrate again and a mixture of SO_2 and SO_3 gases, which is then used to extract the ammonia, the product being a mixture of sulphate and sulphite. If the reactions involved in these methods of using the sulphur from the gas should prove free from mechanical difficulties they would show an appreciable economic advantage, and the future development of such methods will be watched with much interest.

Leaving the question of ammonia recovery from the coal formations, we will now turn for a few moments to an interesting and extremely important phase of the ammonia industry—its synthesis from the nitrogen of the air. At least one method of accomplishing this is familiar to you all; namely, the combination of nitrogen and calcium carbide to form cyanamide and the subsequent distillation of the cyanamide with steam. So far, the cyanamide makers have found it more profitable to sell their product as such than to convert it to ammonia. While the cyanamide industry has had its ups and downs it is, on the whole, developing rapidly, and it is only a question of time when an additional outlet will be sought in the production of ammonia. I understand that an ammonia plant is already contemplated or under way at one of the Norwegian works.

The second method is the direct combination of nitrogen and hydrogen. This reaction is reversible at a temperature of 700° or over and its control has long been sought unsuccessfully. Recently, however, it has been found that at temperatures below the dissociation point of NH_3 and under a pressure of some 175 atmospheres, nitrogen and hydrogen combine in the presence of either osmium or uranium. This process has now been taken up by one of the large German chemical works and is being put on an industrial basis. A pressure of 175 to 200 atmospheres at a temperature of 500°C . looks like a heavy handicap for any process, but I have no doubt that this will be overcome. In their work of fixing atmospheric nitrogen, the company now studying this process has been associated with another of the most famous German chemical houses, and when such a combination as this attacks a problem the history of German chemical research leaves no room for uncertainty as to the outcome. The solution of the problem may come slowly, but it surely will come, and just as the chemical industry is already in possession of at least two really practicable and profitable

methods of making nitric acid from the air, so the problem of the commercial production of synthetic ammonia will also undoubtedly be solved.

There is no danger, however, that synthetic ammonia will mean the decline of the by-product coke oven. The reason is that the world needs pig iron—about ninety million tons of it a year—and every ton of pig means using about a ton of coke. And even though ammonia values should fall, the time is coming when in order to recover the tar and the gas this coke will be produced in by-product ovens. In Germany, the ammonia is already being saved from nearly 90 per cent. of the coal coked, and in England about 60 per cent. of the coke represents coal from which the ammonia has been secured. In America the ammonia is saved from only about 20 per cent. of the coal coked, but in America the conservation movement is, as you know, gathering force daily. We can reasonably expect, therefore, that unless our system of metallurgy is overturned, the by-product coke oven will continue a large factor in the ammonia industry.

At the same time it is also clear that the by-product oven cannot always be the leading factor. If all the coal now coked should be coked in such a way as to save the ammonia, it would, it is true, increase the present output by possibly 60 per cent. This is, after all, only a small increase with which to meet the insistent demand for more ammonia. In the last seven years alone the world's production has nearly doubled and yet there are no surplus ammonia stocks to-day. The ammonia market has absorbed in seven years almost as large an increase in production as could now be gained if all the world's coke were made in by-product ovens.

The demand for pig iron and thus for coke will undoubtedly continue to increase too, but we can hardly expect to maintain the rapid increase of the last twenty years. That period has been one of development, of building new railroads into the West and of replacing stone and wooden bridges and buildings with steel and reinforced concrete. The increase of the next decade must be more nearly commensurate simply with wear and with the increase of population, and the iron trade is already feeling the effects of the great quantities of scrap which are coming back to be re-worked and sent out for further use. The need for ammonia is increasing faster than any coke increase under these conditions can supply. We do not feel this need as yet because most of our soil is still young. Germany feels it though, and the farms of Germany consume some 25 per cent. or more of the world's total ammonia. Japan feels it, and Japan imports every year an amount of ammonia equal to half the entire production of the United States. As the lands become exhausted and population increases the world's demand for ammonia is bound to increase too. And just as the output of the coke oven has outstripped that of the gas retort, so is it probable that the by-product oven must anticipate a time when it in turn will be rivaled or outstripped by other methods of ammonia production.

In a brief way this covers the position of the ammonia industry to-day. The old gas retort is gradually losing ground while the output of the coke oven is increasing by leaps and bounds. Meanwhile, in the manufacture of synthetic ammonia and nitric acid, we seem standing on the threshold of a period of such chemical and electrochemical activity as the world has rarely seen. When we remember that it is only a few decades since ammonia made from camel's dung was still coming into Europe we realize the great strides which the industry has already taken, and the most interesting chapters in its history are apparently still to be written.

ON THE PROPERTIES AND PREPARATION OF THE ELEMENT BORON.¹

By E. WEINTRAUB.

Received March 25, 1911.

I will describe the properties of the element boron isolated in pure fused form in the West Lynn Research Laboratory of the General Electric Company, and also give you in brief the methods used for the preparation of the element and a survey of its possible applications.

It will be best perhaps to first make you acquainted with the properties of the element (author shows a large lump of fused boron and small broken-up pieces, to show the fracture, and also a bottle filled with crushed boron).

Both in appearance and in its curved, conchoidal fracture the lump and the broken-up pieces most nearly resemble black diamond. They are very hard and scratch with ease the known hard substances except diamond. The surface is a very shiny black and takes a beautiful polish.

To my knowledge this is the first artificial product (not an imitation of a natural product) which combines great hardness with an amorphous structure. Boron is, however, inferior to diamond of good quality in its strength. It rubs off rather readily on the diamond lap and even on the carborundum wheel. I do not consider it improbable that in further continuation of the work additional toughness may be imparted to boron and the product become a cheap substitute for black diamond.

I have not determined the melting point accurately, but estimate it to be between 2000° and 2500° C., nearer the second figure than the first.

Boron is a rather volatile element, its vapor tension being appreciable at 1200° C. It can, however, be fused readily not only under atmospheric pressure but also in vacuum.

The properties so far mentioned are in rather good accord with the position of the element in the periodic system. Boron has its place to the left of carbon and has, so to say, right to be hard; conchoidal in its fracture—both properties of fused carbon; and to have relatively high melting point and a vapor tension of such magnitude that it volatilizes to a considerable extent while melting in vacuum.

In fact this similarity of properties might be used to determine in its turn properties of carbon. Thus the high vapor tension of boron would make it probable that the volatilization of carbon at high temperatures (as in incandescent lamps) is a thermal process and not due primarily to electric discharges or chemical processes. The search for a form of carbon having a low vapor tension comparable with that of metals such as tungsten would, in the light of this, be futile and I admit that the argument is weighty enough with me to have caused me to singularly reduce my efforts in that direction.

We come now to a property of boron which is entirely unexpected and places boron in a position all by itself. I refer to its electrical characteristics. When cold, boron is a very poor conductor, its specific resistance being about 10^{12} times that of copper. In this it still shows its similarity to amorphous carbon, which is a very poor conductor, and to diamond, which is an insulator. But where it differs is in the abnormal value of its temperature coefficient of resistance. The resistance of boron very rapidly drops as the temperature rises, so that between room temperature and dull red heat (400°) the resistance drops in the approximate ratio of 2×10^6 to 1. Around room temperature the resistance falls to half its value for every 16° C. In other words, the resistance drops geometrically with arithmetic increase of temperature. The law is, however, only approximate. If extended over large temperature intervals, the interval corresponding to equal resistance ratios increases with the temperature. The relation between temperature and resistance was studied quantitatively up to red heat. When red heat is reached the resistance, however, still continues to drop rapidly.

This enormous influence of temperature on the resistance of boron, combined with the fact that it occurs at ordinary temperatures, makes the behavior of boron as an electrical conductor entirely different from that of ordinary conductors. Thus Ohm's law becomes useless almost to the same extent as in case of gaseous media. In fact the behavior of boron is more like that of a spark gap or arc than that of a solid conductor. There exists, for instance, a "break down" voltage in case of boron as in that of an air gap. Below the break-down voltage only very small current flows through a boron conductor, but once current is started (the air gap is "bridged" over) boron becomes a relatively good conductor.

The potential drop across a boron conductor falls first very rapidly as the current increases, but has a tendency to become constant and is usually approximately constant through quite a range of current. This potential-current curve is again very much like that of a discharge through gases.

The conception of a steady resistance which has the function of preventing the conducting medium from running away is applicable as in the case of arcs.

Similarly to arcs it is impossible without special arrangements to run two or more boron conductors in parallel as one robs the others of current.

¹ Address presented before the Northeastern Section of the American Chemical Society, February 17, 1911.

Before an audience of chemists, these remarks on the electrical characteristics of boron will suffice. To the electrician there is almost an endless variety of surprising phenomena.

Speculation as to the cause of this abnormal behavior of boron might be of interest, but I would like to emphasize only the following point, namely, that the enormous drop in resistance here takes place in an elementary substance, the conductivity of which is wholly metallic. Whatever theory may be proposed for the explanation of the behavior of boron, this fact must be taken as fundamental.

In fact the abnormal value of the temperature coefficient (as well as the high specific resistance) are peculiarly properties of *pure boron*. When foreign elements are added to boron the conductivity increases (in analogy to ordinary solutions) and the temperature coefficient of resistance becomes reduced in value until with a sufficiently large percentage of the foreign element the characteristic properties are entirely obliterated.

Boron presents a very grateful case for exact measurements, as the drop in resistance occurs at ordinary temperatures, and it would be very desirable to determine the temperature resistance curve with great accuracy. The curve thus obtained would be of theoretical interest and could also be used as the basis of a very delicate method of temperature measurements.

It would also be interesting to determine the law connecting the resistance of boron and its negative coefficient of resistance with the amount of foreign elements, such as carbon, magnesium, etc., added. The effect of these additions is very large and I have determined it with only an accuracy sufficient for technical purposes, but it would be interesting to find out the exact relation between the concentration of the dissolved substances and the conductivity as well as the coefficient of resistance. I am inclined to believe from my experiments that the law is an exponential one.

And now that I am started in the direction of suggesting work for others, I am tempted to make a few more suggestions as to lines of work which I for the immediate present cannot take up.

It would be interesting to measure the heat conductivity of boron at different temperatures and compare it with the electrical conductivity. If the parallelism between these two which holds in the case of metals should hold approximately in the case of boron, then we should expect an enormous increase of the heat conductivity with the temperature.

It would also be interesting to study the specific heat of boron at different temperatures. Weber had at his disposal only impure boron powder and his results must, therefore, be unreliable.

No matter how interesting the investigations outlined would be, there are others of technical nature referring to applications of boron to electrical machinery, telegraphy, etc., which at present require all my attention and I am in the position of a man who is regretting that he cannot find more than 24 hours in a day.

I will now give a brief description of the methods used in the preparation of the element.

We are using two different methods. In the first we start with the reduction of boric anhydride by magnesium. This reaction was carried out by various chemists, beginning with Berzelius, Wohler, etc., and recently by Moissan. I must refer for a description of the results obtained by myself to my article in the *Transactions of the American Electrochemical Society*, Vol. 16, 1909. It will suffice here to state that as a result of a thorough study of the reaction we made one step in advance of the previous workers—we found, that under certain conditions of temperature, proportion of reacting substances, etc., a perfectly homogeneous product is obtained which contains as chemical constituents only boron and oxygen, in proportions very nearly corresponding to the formula B_2O . We called the substance "boron suboxide" without, however, desiring thereby to express a definite opinion as to its chemical nature. At the time this seemed to be an important improvement, as the elimination of magnesium from the final product seemed to be desirable. Further work has shown, however, that in the treatment to which the impure product has to be subjected in order to obtain pure boron it matters little whether the impurity is oxygen or magnesium or nitrogen, etc.¹ This treatment consists in heating the impure boron whether containing boron suboxide or magnesium boride or nitride to a temperature near the melting point of boron. At this temperature all these compounds dissociate, magnesium and nitrogen come off as such, oxygen as boric anhydride.

The main difficulty encountered in the development of this method was that of obtaining on a large scale high temperatures in the neighborhood of 2000° without the use of carbon in any form whatever, as boron has a great affinity for carbon and carbonaceous gases at that temperature.

The second method is based on the decomposition of boron chloride by hydrogen at good red heat. This reaction is carried out in two different ways: (1) in an arc discharge taking place between two boron or water-cooled copper electrodes in an atmosphere of boron chloride and hydrogen, and (2) by deposition on a hot graphite tube heated by current passing through it. The temperature and conditions can be so adjusted that practically no combination takes place between the boron and the graphite and very pure boron can be obtained. Boron chloride is best prepared by passing chlorine over boron carbide, which latter can be made in the electric furnace from boric anhydride and carbon.

I want to add a few words on the possible applications of boron in science and industry.

The first thing that suggests itself is its use for accurate measurement of temperatures. In view of the exceeding accuracy of electrical measurements

¹ The preparation of boron suboxide free from other impurities proved, however, useful in connection with the solution of the problem of producing sound copper castings for the description of which the reader may be referred to the *Transactions of the American Electrochemical Society*, Vol. 18, 1910.

and the rapid change of resistance of boron with the temperature an accuracy in temperature measurements could be obtained which would be greater than anything yet available, especially as the boron resistor could be introduced in form of a very small filament, thus disturbing but very little the thermal conditions. Of course the boron thermometer would have to be calibrated and above red heat it would have to be enclosed in an envelope filled with inert gas.

Closely connected with this would be the use of boron as a temperature regulator in a way so obvious as to require no particular description.

Finally, in the same line of thought, boron could be used for measuring radiant energy. A rough surface of boron would probably behave very nearly like a black body, but if necessary a part or the whole of its surface could be covered with fine carbon. One way in which the measurement of radiant energy could be carried out would be by determining the radiant energy input as a difference between electrical energy inputs before and after the radiant energy falls on the boron piece. The temperature of the boron piece is recognized to be the same by the fact that its resistance is the same. This ought to be a very delicate zero method.

The industrial applications, however, are those which have first claim on my attention. Without going into details, I may say that these are based on the electrical characteristics of boron and on its mechanical properties.

The large drop of resistance with the temperature which transforms boron under certain conditions from a very poor conductor for normal voltages into a good conductor for abnormally high voltages is certain to make it valuable for protection of electrical circuits.

The potential current curve which shows a drop

in potential with increase in current makes possible the use of boron either alone or in connection with an ordinary resistance (so as to give a unit with a constant potential drop) for the purpose of regulating electrical machinery.

The influence of small amounts of other elements (carbon especially) on the specific resistance and temperature coefficient of boron, which was described above, gives a very delicate means for adjusting the boron resistor to any prescribed requirements.

The valuable mechanical property of boron consists, of course, in the fact that it combines hardness with amorphous structure and in the course of our work we have already succeeded in producing meter jewels superior in quality to sapphire.

Will it be possible to approach the properties of diamond or perhaps by combining boron and carbon even exceed diamond in its hardness? I can only say that we are working on this problem.

In conclusion, I wish to attract your attention to the close interrelation of electrical and chemical methods in the work I have tried briefly to describe to you tonight. The investigation was started originally for the purpose of determining whether boron is a suitable element for incandescent lamp filaments. In the course of the investigation, in order to isolate the element, electrical methods had to be used to obtain the high temperatures needed. In fact, the isolation of the pure element is practically impossible without the use of electrical methods, and the failure of previous chemists can easily be explained by the fact that they did not possess the necessary electrical tools. Finally, after the chemical problem had been solved and the element isolated, its main applications have been found again in electrical machinery.

How many other interesting and useful applications may not yet be found in this vast field of electrochemistry in its broadest sense?

ORIGINAL PAPERS.

THE CHEMISTRY OF ANAESTHETICS, I: ETHYL ETHER.¹

By CHARLES BASKERVILLE AND W. A. HAMOR.

Experiences of expert anaesthetizers, not accounted for by idiosyncrasy, obtained in the use of ethyl ethers supplied by various manufacturers in numerous surgical cases,² furnished the motive for this investigation. The standards laid down by the various pharmacopoeias of the world are not uniform. In view of that fact alone, a thorough investigation seemed called for. We have not carried out any physiological experiments, however. Inquiries addressed to large consumers of the solvent in manufacturing processes adduced further need for satisfactory methods of determining the purity of ethyl ether and of detecting impurities introduced, or prov-

ing their absence, if eliminated, in the modification of raw products used in its manufacture. The presence of small amounts of substances has oftentimes been the cause of a chemical reaction proceeding in a particular direction by virtue of a "catalytic action." So the presence of even traces of certain substances, as peroxidized compounds, aldehyde, etc., may have caused some reactions to be incorrectly explained, or to follow an unusual, or unaccounted-for, route.

For convenience, the investigation has been subdivided under the following heads:

1. (a) *The Tests for Odor of Ethyl Ether*; (b) *A Study of its Physical Properties*; (1) *Density*, and (2) *Boiling Point*.

2. *Tests for the (a) Residue*; (b) *Acidity*; (c) *Sulphur and Sulphur Compounds of Ethyl Ether*.

3. (a) *Detection of Water and Ethyl Alcohol in Ethyl Ether*; (b) *Dehydration of Ethyl Ether*; (c) *Tests for*

¹ Read before the New York Section of the American Chemical Society.

² Our attention was specifically directed to the question by Dr. J. T. Gwathmey, of New York City, a member of the Anaesthetic Committee of The American Medical Association.

Alcohol; (d) De-alcoholization of Ethyl Ether; (e) Different Processes for Making Ethyl Ether; (f) Detection of Acetone in Ethyl Ether.

4. On the Changes Occurring in Stored Ethyl Ether.
5. On the Existence of Ethenol in Ethyl Ether.
6. (a) On the Detection of Peroxides in Ethyl Ether; (b) New Tests for the Peroxides; (c) Occurrence of Acetal in Ethyl Ether.
7. (a) Methods for Detecting Aldehydes; (b) Purification of Ethyl Ether from Aldehydes.
8. (a) Scheme for the Examination of Ethyl Ether Intended for Anaesthetic and Reagent Purposes; (b) Degrees of Purity of American Ethyl Ethers Used for Anaesthesia; (c) Value of Chemical Tests for Anaesthetic Ethyl Ether.

In this paper the various grades of ether have been discriminated in accordance with the following classification, which the authors suggest as a basis:

A. *Pure Ether*.—Absolute ether—ether free from all impurities.

B. *Anhydrous Ether*.—Ether free from water, but which may contain traces of ethyl alcohol and acetaldehyde.

C. *Anaesthetic Ether*.—Ether complying with the pharmacopoeial requirements. Such ether may contain ethyl alcohol (up to 4 per cent.), and traces of acetaldehyde, acids, and water, although, in the opinion of the authors, it is highly desirable that the three last mentioned—i. e., the impurities—be totally eliminated.

D. *Commercial Ether*.—Ether which contains at least 95 per cent. by weight of ethyl oxide.

All other grades of ethyl ether should be classed as *Impure Commercial Ether*.

The purity of laboratory ether, or ether intended for analytical purposes, is entirely dependent upon the purpose for which it is intended. For ordinary reagent purposes, the grade specified under *Anaesthetic Ether* is suitable, and in general may be said to answer all such purposes; but in special cases the other ethers may be employed.

I. THE TESTS FOR ODOR OF ETHYL ETHER AND A STUDY OF ITS PHYSICAL PROPERTIES.

(a) *Odor*.—Pure ethyl ether is a strongly refractive, colorless, transparent, volatile, very mobile, inflammable liquid, with a characteristic exhilarating odor and sharp, burning taste. These properties may be altered more or less by the presence of impurities, however, and this applies particularly to commercial ether, which often contains substances giving rise to a foreign or evil odor. These substances are generally the result of impurities present in the alcohol employed in the manufacture of the ether or they are produced by various decompositions which occur; yet, as in the cases of other chemicals, there are instances of sophistication, although these are comparatively rare. There are more frequent instances of contamination resulting either from the lack of control in the manufacture or from careless storage. It is almost needless to call attention to the necessity for having a substance such as ethyl ether, which is

used so extensively in the most critical cases, as pure as human ingenuity can provide it.

Traub¹ pointed out that a sample of "impure" ether usually leaves a fruity odor² when allowed to evaporate on filter paper, and it is generally recognized that filter paper which has been moistened with ether must possess no odor on the evaporation of the latter. This test is given in the pharmacopoeias of Austria, Belgium, Japan, Switzerland, Spain, Great Britain, Germany, and the United States. Generally a positive result may be said to be indicative of the presence of "heavy oil of wine,"³ amyl, propyl or butyl compounds, or fusel oil. However, neither the British Pharmacopoeia nor the German Pharmacopoeia states the quantity to be used for the test, while the United States Pharmacopoeia specifies that 10 cc. of ether shall be poured in portions on the blotting paper. These three pharmacopoeias require that the paper, after drying to express the ether, shall possess a neutral nature. At the time indicated in the case of important improvement, copoeia,⁴ the test for odor required from the final product, since fusel oil, if present, as work has shown, may excite coughing during its use, to which the impure ether, as well as that of "heavy oil of wine," is intended for analytical purposes, the impurity is oxygenated, etc.⁵ This treatment for anaesthetic purposes rarely impure boron whether paper on evaporation, cast magnesium boride or which show the necessity for the melting point of test for odor.⁵

When testing for odor, thitrogen come off as such, papers has been suggested, say 25 cc., added in portions entered in the development of the two inside papers out, with obtaining on, should be perceptible. neighborhood

We have found that the test may be satisfactorily made as follows: The ether is well shaken in the container, and then 25 cc. are allowed to evaporate spontaneously on a filter paper 10 cm. in diameter, contained in a flat porcelain dish. The ether is added in portions of several cc. in such a manner as to completely moisten the paper; and in case the odor is doubtful or confirmation is necessary, a portion of 50 cc. of the sample is allowed to evaporate, it being added to the filter paper in small amounts as above.

¹ Pharm. Z. Russland, **31**, 504.

² Probably due to the presence of propyl compounds.

³ In this paper, the term "heavy oil of wine" is held to signify the oil which passes over if the temperature is raised after the preparation of ethyl ether. Liebig [*Handw. d. Chem.*, **1**, 223 (1857)], who found that it passes over when sulphur dioxide and olefin gas are given off, regarded "heavy oil of wine" as an ethyl sulphate of "etherol." According to Claesson (*J. prakt. Chem.*, **19**, II, 259) and Serullas (*Ann. chim. phys.*, **39**, II, 152), it consists of ethyl sulphate mixed with olefines. The composition varies materially, and the phrase is indefinite and rather vague; but it is considered that the yellowish oil of a penetrating odor (sp. gr., 1.095 to 1.13) procurable in the manufacture of ethyl ether, is a possible contaminant of the latter, and the term "heavy oil of wine" is therefore used by way of distinction.

⁴ See the suggestion of the British Pharmacopoeia Committee of Reference in Pharmacy, *Chem. and Drug.*, **69**, 862.

⁵ For instance, see Ohliger, *Proc. Mich. Pharm. Assn.*, **1906**, 47. Other cases will be referred to under "Tests for Residue," where a supplementary test for odor is given. It should be mentioned here, however, that many samples of the best "methylated ether" leave a distinct and pungent residue.

No foreign odor should be perceptible, especially as the last portions of the ether disappear. If a decided odor is imparted to the filter paper, the ether should be rejected, but for further information may be tested for such impurities as "heavy oil of wine," fusel oil, or petroleum spirit. The nature of the impurity in this case is often indicated by the odor itself; for instance, when fusel oil is present to the extent of 0.1 per cent., it may be distinctly recognized by the amyl odor (fusel oil contains 44-71 per cent. of amyl alcohol) which is imparted to the paper.¹ The occurrence of this substance and of "heavy oil of wine," as mentioned before, is rare in the case of anaesthetic ethers² and they are really only likely to occur in commercial and impure commercial ethers. Adrian³ found that ether containing "oil of wine" becomes turbid on shaking with water, and this is the only direct test which has been suggested for the detection of that impurity.

It could be carried out by a method which may be employed for the determination of the specific gravity of petroleum ether, an unusual energy input before, and improbable now.

falls on the boron piece.—1. Density. Ether, when a boron piece is recognized, possesses a specific gravity that its resistance is 1.19 at 15°/4° C.; but if it is very delicate zero method, its rectification, drawn off

The industrial application stored, the specific gravity which have first claim on. The purest ether procuring into details, I may 0.718-0.719 specific gravity the electrical characterist water on exposure to the chemical properties. 0.720-0.721 specific grav-

The large drop of resistance of steadiness. An ether which transforms boron specific gravity of 0.720 may from a very poor conductor being decanted several times, and conductor for a solution of water in contiguity to and on make it valuable. Nowing ether has been the cause of a good many differences between purchaser and dealer, since ether which left the works with a specific gravity of 0.718-0.720 may, after repeatedly opening the bottles, drawing off, etc., absorb moisture and rise to 0.721.⁶ When anhydrous ether is exposed to normal air directly for 30 minutes at 25° C., it absorbs moisture and the specific gravity may rise 0.002 of a point; longer exposure results in a greater increase, which may be as much as 0.004 after exposure for several hours at the room temperature.

Since the specific gravity of ether is 0.7178 to 0.719 at 15° C., those requiring ether of 0.720 specific gravity thus allow minimum amounts of water and alcohol. Unless the ether is dried carefully by means of sodium, for example, and is kept constantly dehy-

¹ The strength of the so-called fusel oil smell is not dependent on the quantity of the fusel oil present, but on the presence of odorous constituents. Amyl alcohol, if present in appreciable amounts, may also be detected by slowly distilling 100 cc. of the ether until about 5 cc. remain, and then distilling this residue with sulphuric acid and potassium dichromate, when valeric acid is obtained. An apple-like odor of valeric aldehyde is first produced; this is followed by the peculiar odor of valeric acid.

² Of ten samples of ethers of anaesthetic grade examined by the authors, none imparted an odor to filter paper after evaporation.

³ *Mon. Sci.*, **44**, 835.

⁴ L'Orosi, **8**, 8; *Chem. News*, **53**, 69.—On the Estimation of Ether in the Presence of Petroleum Ether, see Richmond, *Analyst*, **24**, 201.

⁵ In this connection, see *Pharm. Ztg.*, **1892**, 56.

⁶ This has been discussed by Klar, *Chem. Ind.*, **19**, 141.

drated by storing over such an agent, or great care is taken in storing it after final rectification, it is practically impossible to maintain the specific gravity originally possessed by the ether.

The ethers recognized as official by the pharmacopoeias of various countries possess specific gravities as shown in the following table.

The specific gravity of ether should be determined preferably at 15° C. This temperature is more suitable than 25° C., on account of its volatility. The density of so volatile and hygroscopic a liquid as ether, which is so very sensitive to changes of temperature, is very difficult to determine with accuracy, and careful analysts have often obtained divergent results on the same sample; but as the constant is indicative of the strength and purity of ether, it should always be made. For this purpose the pycnometer should be employed, and the form designed by Perkin² possesses advantages over the Sprengel pycnometer for the determination of the density of such a volatile liquid. The Mohr-Westphal balance will serve to give a quick approximate determination, but should not be depended upon where any considerable degree of accuracy is desired. The specific gravity of ether intended for anaesthesia should not exceed 0.720 at 15° C., providing an ether containing minimum quantities of alcohol and moisture is required;³ however, an ether which shows a specific gravity of 0.7215 (2 per cent. absolute alcohol), 0.7228 (3 per cent. absolute alcohol) or even 0.724 (4 per cent. absolute alcohol),⁴ providing the sole "impurity" is ethyl alcohol, is acceptable for anaesthetic purposes according to various pharmacopoeias. Ethyl alcohol serves, it is asserted, as a preservative for ether when the latter is properly stored; and small amounts interfere in no way with the application of ether in anaesthesia. However, the presence of alcohol is unnecessary except when ether is administered by the "drop method." In this case, the presence of alcohol prevents too rapid volatilization and consequent chilling of the apparatus with which the ether is administered. Some have maintained that pure ethyl ether is unsuitable for anaesthesia, but it is a fact that the vapor from ether containing alcohol, when passed through water at 40° C., whereby the alcohol is removed, may be and is being used with great success for anaesthesia. The presence of excess moisture should be guarded against, since ether in contact

¹ No reference is made in the table to ether intended for manufacturing purposes—that is, in the wet process of photography, in the manufacture of smokeless powder, and as an industrial solvent.

² *J. prakt. Chem.*, N. F., **31**, 486.

³ Ether possessing a density of 0.7202 contains 1 per cent. of ethyl alcohol of 0.82 specific gravity; and the ether of the German Pharmacopoeia possessing a specific gravity of 0.720 contains 0.1 per cent. water and 0.8 per cent. alcohol. Bein (*Abh. Kais. Normal-Eichungs-Kommission*, **1908**, VII, 1-42; *Chem. Zentr.*, **1908**, II, 1994) conducted determinations of the expansion of pure ether (density 0.720) and of mixtures of the same with 5 and 10 per cent. of 90 vol. per cent. alcohol, and of commercial ether by the dilatometric method of Kreittling. The results he obtained are given in numerous tables. Bein also worked out a table which permits of the reduction to standard temperature of density determinations on mixtures of ether and alcohol made at temperatures other than 15° C.

⁴ It may generally be assumed that ether of 0.724 specific gravity contains 95.9 per cent. absolute ether, 3.72 per cent. absolute alcohol, and 0.38 per cent. water (*Pharm. Centralh.*, **1894**, 118). Such ether should always be tested for the presence of other impurities, however.

Specific gravity.*	0.716 — 0.717. ¹	0.720.	0.720 — 0.722.	0.725.	0.724 — 0.728.	0.728.
Countries where recognized....	United States ²	Russia Great Britain ³ Mexico ⁴ Spain ⁵ Japan ⁶ Germany ⁷ France ⁸ Belgium ⁹ Sweden ¹⁰ Holland ¹¹ Hungary ¹²	Switzerland ¹³ Italy ¹⁴ Norway ¹⁵ Denmark ¹⁶	Austria ¹⁷	Finland ¹⁸	Portugal ¹⁹

* For values for every 5° from 0° to 195°, see Ramsay and Young, *Phil. Trans.*, **178**, 85. Buchan (*Chem. News*, **51**, 94) found that ether possessed a specific gravity of 0.7197 at 15°; Squibb (*Ibid.*, **51**, 67, 76), 0.71888 at 15°/4°; and Oudemans (*Ber.*, **19**, ref. 2), 0.7192 at 15°. For various determinations, see Clarke's "A Table of Specific Gravity for Solids and Liquids," **1888**, pp. 176-97. Krauch ("The Testing of Chemical Reagents for Purity," **1902**, p. 92) gives the specific gravity of *Aether puriss.* as 0.720, and that of ethyl ether, free from water, distilled over sodium, as 0.718 to 0.720. For determinations from 1816 to 1903, see *Wissenschaftliche Abhandlungen der Kaiserlichen Normal-Eichungs-Kommission*, **1908**, VII, p. 20. It is to be hoped that all the pharmacopoeias will adopt 15° as the standard temperature at which to determine specific gravity (international hydrogen scale), and consider the unit of expression in every case the specific weight of water at 4°. While it is true, as indicated by Stevens (*Proc. Mich. Pharm. Assoc.*, **1906**, 96), that the change in the temperature for taking specific gravities from 15°/15° to 25°/25° appears to have met with approval among the pharmacists of this country, and while the differences between specific gravities as compared with water at 15° and 4° are so slight that for practical purposes they can be neglected (see, in this connection, Schimmel's *Semi-Ann. Rept.*, **1906**, Oct.-Nov., p. 85), yet the temperature 15°/4° is more scientific and has been universally adopted by those engaged in pure research and by commissions on physical standards.

¹ At 25°/25° C. All other values are at 15° C., the standard temperature.

² The *Pharmacopoeia of the United States of America*, 8th revision 1905, p. 31. Ether of the specific gravity 0.750 at 15° was the only grade recognized by the U. S. Pharmacopoeia until the fourth revision (1860), when "aether fortior," density not exceeding 0.728, was introduced. In the sixth revision of the Pharmacopoeia (1880), the specific gravity of "aether fortior" was changed to not exceeding 0.725 at 15°.

³ Ether of the specific gravity 0.735 has been official in Great Britain for many years, but foreign pharmacopoeias only recognize the fluid which is official in the *British Pharmacopoeia* as "Aether Purificatus." The latter is identical with the "Aether pro narcosi" of the German and Swedish Pharmacopoeias. In 1893, Dott (*Pharm. J. and Trans.*, **23**, 617) suggested that the specific gravity of the official ether of the *British Pharmacopoeia* should be altered to "not exceeding 0.724." The following ethers are used in Great Britain:

1. From Pure Rectified Spirit.

(a) *Aether* (off.). Sp. gr., 0.735. "Ordinary medicinal ether." Occasionally employed as an anaesthetic, but is not so suitable for inhalation as—

(b) "Aether Purificatus" (Off.). Sp. gr., 0.720-0.722 (*British Pharmacopoeia*, **1898**, p. 26).

2. From Methylated Spirit.

(c) "Absolute Ether." Sp. gr., 0.717-0.719. Said to be not adapted for general anaesthesia.

(d) "Rectified Ether." Sp. gr., 0.720. Reported as being adapted for producing general anaesthesia.

(e) "Methylated Ether." Sp. gr., 0.730. Employed for common purposes.

Opinions are still divided as to the relative merits of (b) and (d). Hewitt ("Anaesthetics and Their Administration," **1907**, p. 22) states that while it may be regarded as highly probable that the purer ether possesses slight advantages over the methylated, the latter, if carefully prepared by a recognized manufacturer, is certainly quite suitable for hospital use. Richardson (*Med. Times and Gaz.*, April 9th, 1870) decided in favor of "methyl ether" for rapid anaesthesia.

⁴ *Nueva Farmacopoea Mexicana*, **1904**, p. 521.

⁵ *Farmacopoea Oficial Espanola*, 7th ed., **1905**, p. 282.

⁶ The *Pharmacopoeia of Japan*, 3rd ed., **1907**, p. 25.

⁷ *Deutsches Arzneibuch*, 5th revision, **1910**, p. 34. For a discussion of the different grades of ether in use in Germany at various times during the past century, see Arends, *Pharm. Ztg.*, **41**, 662. The density given refers to "narkoseäther."

⁸ *Codex Medicamentarius Gallicus Pharmacopoei Française*, **1908**, p. 245. According to Squire ("Companion," 18th ed., **1908**, p. 103), ether of density 0.724 is also official in France.

⁹ *Pharmacopoea Belgica*, 3rd ed., **1906**, p. 15.

¹⁰ *Pharmacopoea Suecica*, 9th ed., p. 20. The constant given is that re-

with water, or moist air, gives rise to various impurities of an objectionable nature.

2. Boiling Point. Ether is very liable to present the appearance of boiling at temperatures both above and below its true boiling point, so that this constant is not a very dependable indication of the strength in practice. Then, the boiling point presents smaller differences than the density and is more difficult to determine accurately.²¹ On the other hand, although the boiling point of ether purified by different methods is constant, the density is not.²² This applies, of course, only to highly purified ether, since an ether which has a boiling point of 34.50° C. may, when fractionated in the presence of water, form a binary mixture boiling at 34.15° C. Moreover, the boiling point of ether and that of the mixture with water are raised by the presence of small amounts of alcohol; and the presence of considerable amounts of the latter may be approximately determined by accurate fractionation.

Although the boiling point of pure ether is 34.6° at 760 mm., there are no ethers of anaesthetic grade on the market which comply fully with this requirement, owing to the mutually opposing influences of water and alcohol on the boiling point, and only ether distilled over sodium closely approximates it. Since, therefore, these influences render the constancy of the boiling point as ordinarily determined of little or no use as a criterion of purity, it is sufficient to require that ether shall commence to distil at a temperature not under 34° C., and that is, shall possess a boiling point of 34°-36° C. We have found that ether purified by distillation over sodium yields a distillate amounting on the average to 99.50 per cent. of the total amount taken when fractionated,

quired for "narkos ether;" ether of the density 0.720-0.722 is also official. In 1888, it was specified that the density should not exceed 0.725.

¹¹ *Pharmacopoea Nederlandica*, **1905**, p. 27.

¹² *Pharmacopoea Hungarica*, **1909**, p. 18. The density given is that specified for "aether pro narcosi;" that of "aether depuratus" is stated to be "to 0.723."

¹³ *Pharmacopoea Helvetica*, 4th ed., **1907**, p. 25.

¹⁴ Squire (*loc. cit.*). The *Farmacopoea Italiana* (Orosi), 4th ed., p. 1375, gives 0.723.

¹⁵ Ewald's "Handbuch der allgemeinen und speciellen Arzneiverordnungslehre," **1898**, p. 168. The *Pharmacopoea Norvegica*, **1879**, p. 16, the latest edition we have seen, specifies "not over 0.725."

¹⁶ *Pharmacopoea Danica*, **1907**, p. 31. 0.720 ether is also official.

¹⁷ *Pharmacopoea Austriaca*, **1889**, p. 16; the latest revision available.

¹⁸ *Pharmacopoea Fennica*, 4th revision, p. 20. Ether of this density is also specified in the *Pharmacopoea Croatica-Slavonica*, **1888**, p. 40; and it was official in Russia in 1880. However, the latter adopted the value 0.720 in 1891.

¹⁹ Squire, *Loc. cit.*

²⁰ These will be referred to under "Peroxides" and "Aldehyde."

²¹ Squibb, *Chem. News*, **51**, 66.

²² Concerning this point, see Wade and Finnemore, *J. Chem. Soc.*, **95**, 1842.

this percentage distilling off between 34°–35° C., whereas three ethers used for anaesthesia gave the following results:

Temperature.	Percentage by volume.		
	I.	II.	III.
	Per cent.	Per cent.	Per cent.
25°–34°.....	1.00	1.00	1.00
34°–36°.....	98.50	97.00	97.50
36°–37°.....	0.50	2.00	1.50
37°–42°.....

In view of these facts, augmented by other experiments, we are of the opinion that ether intended for anaesthetic purposes should, when carefully fractionated, yield a distillate amounting to at least 97 per cent. by volume between 34° and 36° C., and that not more than 1 per cent. shall distil off below 34° C. In case more than very slight traces of acetaldehyde are present, or if methyl ether or methyl-ethyl ether is contained in the ether, the amount which distils off below 34° C. may be increased considerably, and, in this event, the distillate should be examined further, in order to ascertain whether the ether should be rejected.¹ If more than mere traces of aldehyde are present, the ether is unsuitable for anaesthetic purposes (see discussion under "Aldehyde"); and, although methyl ether or methyl-ethyl ether would not interfere with the anaesthetic value of the ether, according to the experience of English anaesthetizers, their presence is not desirable. We might suspect their presence as an impurity in ethers on the American market if they were made from methylated spirit, but this is rare now.²

Boiling point. ³	34.5°.	34°–36°.	35°.	35.5°.	35°–36°.	36°.	36.5°.
Where recognized.....	Great Britain. ⁴	Finland. Austria.	Hungary. Japan. Germany. Belgium. Russia.	United States.	Switzerland.	Italy. Norway. Denmark. Portugal. Holland.	France.

¹ Cf. Cowie, *Pharm. J.*, 1908, ii, 366, 407, who considered that the boiling-point determination is a most reliable test, showing the presence or absence of methyl ether, alcohol, water and acids in one step.

² Ether made from methylated spirit contains, according to some authorities, a considerable quantity of gaseous methylic ether in solution, which lowers the specific gravity and boiling point (Abraham, *Chem. and Drug.*, 41, 520); and it has been stated that 10 per cent. of methylated ether may be detected by its commencing to boil at a lower temperature than ether prepared from rectified spirit. By removing the distillate immediately the thermometer indicated 90° F. Jones (*Pharm. J. and Trans.*, 16, 663) obtained the following results with various British ethers:

100 cc. taken.	Cc. obtained.	Remarks.
Rect. ether, 0.720	0	
Rect. ether, 0.730	0	
Meth. ether, 0.717	60	Boiled freely at 74° F.
Meth. ether, 0.720	54	
Meth. ether, 0.730	23	

As mentioned under "Density," three grades of ether prepared from methylated spirit are used in Great Britain. One of these (sp. gr. 0.717–0.719) is not adapted for general anaesthesia, being an impure article, and it has been stated that it owes its low gravity to the presence of dissolved methylic ether. Allen [*Commercial Organic Analysis*, 1, 181, (1908)] has pointed out that owing to the extreme volatility of methylic ether, ether made from methylated spirit would be practically pure ethyl ether, were it not for the presence in it of other constituents of wood spirit. This is undoubtedly true from a general standpoint, but nevertheless methylic ether has usually been considered to exist in solution in ether prepared from methylated spirit, as determined by an observation of the commencement of boiling. Williamson (*Ann.*, 81, 79; see also Norton and Prescott, *Am. Chem. J.*, 6, 244) found that methyl-ethyl ether is formed together with methyl and ethyl ethers by the etherification of a mixture of methyl and ethyl alcohols by sulphuric acid; and, since methyl ether boils

In the case of anaesthetic ethers and ethers intended for special analytical purposes, none of the sample fractionated should come over above 37°; but it appears in the case of ether intended for industrial purposes, that it is sufficient that at least 98 per cent. shall distil off below 42° C.⁵

When the first mentioned are fractionated, there should be no residue remaining in the fractionating vessel after a temperature of 37° C. is reached; but in the case of the ethers suitable for manufacturing purposes, less than 0.002 per cent. of residue should be left after maintaining a temperature of 100° C. for one hour.

For conducting the fractional distillation of ether, the regulated temperature still-head is the most suitable, but ether may be fractionated with sufficient accuracy by means of more generally available apparatus. It is only necessary to employ a globular glass flask which is provided with a long, yet wide, still-head, and use great caution that the ether vapor does not become superheated. Steam under ordinary or increased pressure may be used as a source of heat, but the distillation may be more easily regulated by means of a naked flame, and, better still, and with more safety, by an electric heater. The thermometer which is used should be carefully calibrated and a little absorbent cotton wrapped around the bulb. If such a precaution is taken, superheating may be avoided.

Ethers recognized as official by various countries possess the following boiling points:

II. ETHYL ETHER; TESTS FOR (a) RESIDUE, (b) ACIDITY, (c) SULPHUR AND SULPHUR COMPOUNDS.

(a) *Residue*.—A test of great importance in the examination of ether is that for extractive matter, in which the deportment with indicators and the

at –34°, and methyl-ethyl ether between 10° and 13°, the latter is likely to occur in larger amounts than the former in ether prepared from methylated spirit.

Ethers on the American market—that is, those manufactured in the United States from rectified spirit or from denaturant formulas authorized by the Commissioner of Internal Revenue—are, so far as we have been able to ascertain, free from methylic ether, methyl-ethyl ether, and American ethers are not contaminated with these substances, formaldehyde or formic acid.

³ According to Beilstein [*Handbuch der Organischen Chemie*, 1, 293 (1893)], the boiling point of ether is 34.97° (34.6° at 762 mm.). Landolt-Börnstein (*Physikalisch-Chemische Tabellen*, 1905, 816) and Seelig (*Organische Reaktionen und Reagentien*, 1892, 106) state that the boiling point is 35°. Krauch (*loc. cit.*) states that ether boils at 34°–36°. For determinations from 1816 to 1903, see *Wissenschaftliche Abhandlungen der Kaiserlichen Normal-Eichungs-Kommission*, 1908, VII, p. 20. These determinations range from 34.2° to 35.7° at 760 mm., but it is well established that the constant is 34.6° at this pressure.

⁴ The British Pharmacopoeia gives the boiling point of ordinary ether as below 40.5°. It does not give a boiling point for "Aether Purificatus," but requires that ether should commence to distil below 34.5°. The Ph. Brit. Committee of Reference in Pharmacy has suggested that ether should distil at a temperature not under 34° (vide, *Chem. and Drug.*, 69, 862).

⁵ Cf. U. S. Navy specifications for the purchase of ether

odor are also to be observed. This test may be given as follows:¹ On the spontaneous evaporation of 20 cc. of ether in a glass dish, the moist residue² must possess no odor, and must neither redden nor bleach sensitive light blue litmus paper. While it is well known that litmus is not a most sensitive indicator, it appears to answer the demand in this case. The moist residue must evaporate completely on the water bath.

The Pharmacopoeias of Sweden, Switzerland, Hungary, Japan, France, Belgium, Great Britain, Germany, and the United States specify a test for residue, but in general it may be said that the pharmacopoeial test for extractive matter is less complete than that given above. Both the United States and German Pharmacopoeias require that ether shall leave no residue on evaporating, but the latter states that when allowed to evaporate at ordinary temperature, ether leaves a damp ring which should not redden blue litmus paper.

The *National Standard Dispensatory* (1905, p. 111) is more specific than the United States Pharmacopoeia for it states that "there must be no fixed residue on evaporation." In general, it may be said that this test is made at ordinary temperatures for acidity (Switzerland, Japan, Belgium, and Germany), but in the Hungarian Pharmacopoeia it is stated that there should be no residue on evaporation; being identical with the method recommended in the United States, and in the French Pharmacopoeia, it is specified that there shall be no residue non-volatile at 100°. The Belgian and Japanese Pharmacopoeias specify 20 cc. when *aether pro narcosi* is being examined, and at least this amount should always be used.³ In most cases too small an amount of the ether is evaporated, and 50 cc. are to be preferred to smaller quantities.

Samples of ether of pharmacopoeial strength have been known to yield a residue on evaporation⁴ and there are cases where ether has been contaminated through carelessness in manufacture⁵ and storage.⁶

Anaesthetic ether should leave no weighable residue after evaporation in a platinum dish at 100° C.

It is appropriate in this connection to refer to a

¹ Thoms (*Ber. d. Pharm. Ges.*, 1894, 240) was the first to specify a complete test for residue. Krauch ("The Testing of Chemical Reagents for Purity," 1902, 93) gives a test similar to that mentioned above.

² In this test, a film of moisture will be found on the dish after the evaporation of the ether. This is due to the attraction of moisture from the air. In this connection, see White, *Pharm. J.*, [iv] 25, 780.

³ Wobbe (*Apoth.-Ztg.*, 18, 458, 465, 487) recommends using 20 cc. when ether for anaesthetic purposes is being examined.

⁴ Patch (*Proc. Am. Pharm. Assn.*, 54, 337) found that a sample of ether, sold as 90 per cent., contained only 74 per cent.; that two samples of U. S. P. strength possessed an acid reaction and yielded a residue; and one sample answering all other tests gave a brown residue.

⁵ It sometimes happens that a small amount of zinc chloride, used as a flux in soldering ether "tins" by manufacturers, is introduced accidentally in the ether.

⁶ For example, Feist (*Apoth.-Ztg.*, 25, 104) has reported a peculiar case of ether contaminated with vanillin. The ether was found to have been unsatisfactory for anaesthetic purposes, so it was examined according to the *Arzneibuch f. d. Deutsche Reich*, 1900. On evaporating 100 g., there was left behind a small crystalline residue, which was identified as vanillin. It appeared to have been introduced by the stoppers in the containers, and illustrates the carelessness prevalent in some apothecary shops.

test which has been suggested¹ and is sometimes recommended² for the detection of various organic impurities in ether—for example, fusel oil, empyreumatic oily matter, and resinogenous bodies in general. The test is, that ether should give a colorless solution when carefully dissolved in pure concentrated sulphuric acid in the cold; and it may be applied as follows: 20 cc. of the sample under examination are added, drop by drop, to 20 cc. of pure concentrated sulphuric acid, which is kept cool during the test and which is contained in a glass-stoppered bottle previously rinsed with concentrated sulphuric acid; and the sulphuric acid is gently shaken after the addition of each drop of ether in order to insure perfect solution. After the equal amounts of ether and acid have been mixed thoroughly, there should result no coloration.

We have found that no ethers of anaesthetic grade now on the market give a positive response to this test, and it is really superfluous when anhydrous or anaesthetic ether is being examined. It is an important test, however, for the presence of various organic impurities (isobutyl, allyl, tertiary butyl, tertiary amyl, methyl and isopropyl alcohols, aldehyde, acetal, acetoacetic ether, and acetone, alone or in mixture, in the presence of furfural, all of which may occur from the use of impure alcohol) in commercial and high-gravity ethers, and should be applied when they are being examined. Even ether of 0.735 specific gravity should give no coloration with an equal volume of sulphuric acid.³ It should be mentioned that it is easy to arrive at false conclusions from this test if the ether under examination is contained in a cork-stoppered bottle, since the extract from the cork or luting may give a decided reaction.

(b) *Acidity*.—Sulphurous and acetic acids were the earliest recognized contaminants of freshly distilled ether. The formation and occurrence of these were studied by Dollfuss;⁴ and Higgins,⁵ Scheele,⁶ Woulfe,⁷ and Pelletier⁸ investigated the purification of ether from these acids. In 1782, however, Scheele⁹ considered that he had proved that "vitriolic acid" is a constituent part of "vitriolic ether," although he was forced to admit that "this small quantity of acid is so insignificant in rectified ether, that is, cannot be maintained with certainty that there exists no aether at all without some mineral acid;" and until 1800, when Valentin Rose¹⁰ showed that the name "sulphuric ether" is a misleading one, since this substance does not, when pure, contain any sulphur or sulphuric acid, sulphuric acid was regarded as a constituent of ethyl ether, and not until after this time were active measures taken to prepare ether in

¹ Traub, *Pharm. Z. Russland*, 31, 504.

² For instance, by the *National Standard Dispensatory*, 1905, p. 111.

³ "On the Physical Properties of Mixtures of Ether and Sulphuric Acid," see Poind, *Proc. Chem. Soc.*, 26, 341.

⁴ "Pharmaceutisch-Chemische Erfahrungen."

⁵ "Minutes," 72.

⁶ "Essays," 1786, 301.

⁷ Thomson's "System of Chemistry," 2, 229.

⁸ "Memoires," 1, 316.

⁹ *Loc. cit.*

¹⁰ *Scher. J.*, 4, 253.

large quantities absolutely free from acids. It was then learned that ether contaminated with sulphurous, sulphuric, and acetic acids could be purified by means of an aqueous or alcoholic solution of potassium or sodium hydroxide; or, as Woulfe proposed, by means of slaked lime; or, as Pelletier and Dize suggested, by means of manganese dioxide. It was also ascertained that washing with water removed considerable of the acidity possessed by crude ether; but it was not known until a later period that the sulphonic acids and their derivatives, formed in the manufacture of ether, are present in some commercial ether and that they may also be extracted by washing with water.¹

It has only been in the last twenty-five years that serious attention has been given to the detection of acids in ether, with the object of devising delicate and reliable tests for acidity and even now there are improvements advisable.

The tests for acidity specified by the various pharmacopoeias may be divided into two classes:

1. Those in which it is stated that the color of light blue litmus paper moistened with water should not be changed to red when the paper is immersed in ether for a certain definite period (ten minutes—Pharmacopoeias of Great Britain and the United States). Some writers, however, state that ether should produce no change in wet blue litmus paper after contact for even 24 hours.²

2. Those in which the ether is agitated with water, after which the latter must show no acid reaction (Pharmacopoeias of France, Hungary and Austria).³

It is generally recognized, therefore, that a test should be applied for acidity, although in some cases⁴ it has been merely stated that the ether under examination should be acid-free and no specific test is given. However, it is necessary to determine the percentage of acidity, in order that the actual amount of acidity may be ascertained and so that definite specifications for ether of various grades may be had. Especially is this requisite in the case of ether for manufacturing purposes, where it is often required that the percentage of acidity shall not exceed a certain amount.

Purchasers of ether in the past have often complained of ether which contained sulphuric acid. It was found that water, on being shaken with such ether, not only showed a strong acid reaction, but also gave a heavy white precipitate with barium chloride. Such unusual contamination can, of course, only be possible in commercial ethers; but small amounts of free acid are likely to occur in ether intended for medicinal and analytical purposes, although any

such serious contamination has become rare, mainly owing to the fact that ether distilled over sodium may be readily purchased or prepared. Such ether is very pure. When it was first introduced, chemists, on testing it, were surprised to find that such ether turns moist litmus blue, yet does not redden phenolphthalein. This deportment of ether distilled over metallic sodium was referred to by Klar;⁵ and Thoms⁶ found that ether, most carefully purified, is not neutral to litmus paper, but gives a bluish tint to sensitive red litmus paper. It has been asserted that the vapor of pure ether reacts alkaline to litmus paper.³ This is not in accord with our experience. We found that when pure ether was allowed to slowly evaporate (20 cc. in five days), delicate red litmus paper supported in the liquid and vapor failed to turn blue, but that part of the paper passed between the glass stopper and neck of the flask did acquire a blue color. This we attributed to the alkali in the glass.

Anaesthetic ether should readily comply with the requirement recommended by Vulpius,⁴ who stated that when 10 cc. of the ether under examination are shaken with some water and 0.1 cc. of decinormal potassium hydrate, there should result a red color in the presence of a trace of phenolphthalein. This test for acidity may be elaborated as follows:⁵ On shaking 20 cc. of ether with 10 cc. of water and 2 drops of phenolphthalein solution, the same depth of color must result on adding an equal amount of *N*/100 alkali as in a test using an equal amount of water alone. In this manner, the acidity of ether may be determined, or the relative acidity as compared with an ether of known purity may be found. It is, however, impossible to titrate back with a standard acid solution and obtain accurate results, since, especially in the event that alcohol is present in the ether under examination, slightly alkaline phenolphthalein is decolorized. This may be ascribed to a retardation of the dissociation of the phenolphthalein alkali by the excess of ether or alcohol.⁶

With three samples of anaesthetic ethers,⁷ we obtained the following comparative results for acidity, using the elaborated test of Vulpius and calculating the results in terms of acetic acid:

Sample No.	Grams of acid calculated as acetic in 100 cc. of sample.	
	Gram.	
1.....	0.0006	
2.....	0.00015	
3.....	0.00165	

When 20 cc. of an ether distilled over sodium are agitated with 10 cc. of pure water and 2 drops of a phenolphthalein solution are added, 0.3–0.5 cc. of *N*/100 sodium hydroxide are necessary to produce

¹ Prunier, *J. Pharm. Chim.*, **5**, 513.

² For instance, Buxton ("Anaesthetics," 1907, p. 118). Cf. here the test of the *Deutsches Arzneibuch*, 1910, p. 34; 5 cc. are tested with litmus paper.

³ According to the *Pharmacopoeia Austriaca*, 1889, p. 16, the test is conducted as follows: equal volumes of ether and water are shaken with litmus solution, and the resulting coloration is observed. The *Pharmacopoeia Francaise* specifies that the water be tested for sulphuric acid.

⁴ For example, in the *Pharmacopoeia Svecica*, 1888, p. 13.

⁵ This point is brought out in the U. S. Army specifications for purchase, in which it is stated that ethyl ether should have less than 0.006 per cent. of acidity calculated as acetic acid.

¹ *Chem. Ind.*, **19**, 141.

² *Chem. News*, **74**, 81. For confirmatory evidence, see *Pharm. Centralbl.*, 1895, 41.

³ Wobbe, *J. Soc. Chem. Ind.*, **22**, 1067.

⁴ *Chem.-Ztg.*, **11**, 1246.

⁵ Vulpius, *J. Soc. Chem. Ind.*, **6**, 750.

⁶ In this connection see Cohn, *Z. angew. Chem.*, **19**, 1389.

⁷ These ethers were purchased in the open market, the labels removed and the cans numbered by Dr. Gwathmey, so we had no knowledge of the names of the makers until the work was completed.

a faint, yet decided, alkaline reaction.¹ Using as a standard an ether which required 0.4 cc. of *N*/100 sodium hydroxide to cause a definite alkaline reaction, *N*/100 sodium hydroxide was added to various ethers (20 cc.) after shaking with water (10 cc.), in order to find the acidity. The results were as follows:

Sample No.	Cc. <i>N</i> /100 NaOH equivalent to 0.4 cc. in standard.
1.....	0.75
2.....	0.50
3.....	0.75
4.....	0.75
7.....	1.00
8.....	1.80
9.....	1.50
10.....	0.55

There are reasons for stating, therefore, that the relative acidity of an ether may be determined by comparing it with an ether of known freedom from acids, and that in this manner a standard may be made for ethers for various purposes. For example, on shaking 20 cc. of an ether purified by distillation over sodium, with 10 cc. of water and 2 drops of phenolphthalein solution, the addition of not more than 0.5 cc. of *N*/100 sodium hydroxide should result in the production of a decided red coloration, whereas in the case of ether purified by another method, yet in which considerable purity is desired, the addition of not more than 1.5 cc. of *N*/100 sodium hydroxide should give a decided alkaline reaction. We are of the opinion that when more than 1.0 cc. of *N*/100 sodium hydroxide is required in this test, the ether should be rejected for anaesthetic purposes, and it is highly desirable that such ether should contain no free acid at all.

The results given above serve to show the variability of ethers on the market, even of the same make, for different results were obtained from fresh cans obtained at different times.

When commercial ether is being examined, sulphuric acid or acetic acid may be detected by saturating with an alkaline carbonate, and testing the aqueous solution for sulphate by means of barium chloride solution, or for acetate by means of arsenic trioxide.² In case appreciable amounts are present, the acidity may then be determined in the terms of the acid present. Two other tests which have been proposed for the detection of acidity in ether may be referred to here. Vulpius³ proposed that 5 cc. of the ether be allowed to evaporate until the residue amounts to 0.1 cc.; this residue should then be neutral to litmus paper. Wobbe⁴ recommended that 20 cc. of the

ether be allowed to evaporate after the addition of 5 cc. of water, after which the residue should not bleach nor redden litmus paper. These tests are but modifications of the usual test for residue, and the latter may be supplemented by the test of Wobbe when doubts exist concerning the deportment of the residue towards litmus paper. The test proposed by Vulpius possesses no advantages over the residue test which has been recommended, however.

(c) *Sulphur and Sulphur Compounds*.—Sulphur and sulphur compounds are only likely to occur in quite impure commercial ethers.

De Koninck¹ suggested that free sulphur and organic sulphur be detected by shaking about 10 cc. of the ether with a drop of pure mercury, after which the mercury must retain a clean surface and no black powder should be formed.

Ten Bosch² pointed out that the darkening of mercury is not conclusive evidence of the presence of sulphur, since the same effect is produced by hydrogen dioxide.³ To detect sulphur, he recommended that the black powder be fused with "soda" and "nitre," the fusion treated with nitric acid, and then tested for sulphuric acid with barium chloride. Notwithstanding this, simple agitation with mercury and the production of a dull gray surface on the metal, or the assumption of a gray or black color by the liquid, is frequently given as a test for the presence of sulphur compounds in ether; for example, Krauch and Merck⁴ state that on shaking 20 cc. of ether with a globule of mercury for two minutes in a glass-stoppered bottle, the bright surface of the mercury must not be tarnished nor should a black precipitate form.

We have found that the presence of even 0.2 per cent. of either ethyl sulphide or mercaptan⁵ in ethyl ether, otherwise pure and dry, results in the production of no positive tarnishing of the metal nor the separation of a precipitate, when the ether is agitated with pure mercury; that sulphur dioxide or sulphurous acid, in any likely amounts, give a negative result also; and that only the presence of free sulphur or hydrogen sulphide can produce the reaction generally ascribed to organic sulphur, excepting, of course, hydrogen dioxide, which produces a gray precipitate even when present in mere traces. We have also found that peroxides and ethyl sulphide cannot exist simultaneously in ether.

In view of this, therefore, no reliance can be placed on the test proposed by de Koninck, and we cannot recommend it for the detection of likely amounts of probable impurities; in fact, it is useless.

It is probable that in many cases the presence of sulphur or sulphur compounds has been assumed when hydrogen dioxide or ethyl peroxide actually produced the phenomena observed; but there is another source of error in this test. On agitation with

¹ When 0.5 cc. of a 1:100 alcoholic solution of phenolphthalein is added to 100 cc. of water, 0.5 cc. of *N*/100 KOH is necessary to produce a distinct red color. In this connection see Trommsdorff's table in Büchman's "Chemisch-technische Untersuchungsmethoden der Grossindustrie," 3rd ed.; Cohn's "Indicators and Test Papers," p. 220; and A. A. Noyes, *J. Am. Chem. Soc.*, **32**, 815. It appeared from the last-mentioned investigation that thymolphthalein might be advantageously substituted for phenolphthalein as the indicator in estimating the acidity of ether. It was found, however, that when the former is employed, the color change is less distinct, and that it is less sensitive.

² On the Detection of Acids in Ether by This Method, see Adrian, *Mon. Sci.*, **44**, 835. Cf. also the method given in the *Nueva Farmacopea Mexicana*, 1904, p. 521.

³ *Chem.-Ztg.*, **11**, 1246.

⁴ *Apoth.-Ztg.*, **18**, 458.

¹ *Z. angew. Chem.*, **89**, 4; *Z. anal. Chem.*, **28**, 696; *Pharm. Ztg.*, 1891, No. 33.

² *Nederl. Tijdschr. voor. Pharm.*, April, 1889, 113.

³ The occurrence of this substance in ether will be referred to later.

⁴ "Chemical Reagents, Their Purity and Tests," 1907, p. 101.

⁵ On another test which could be applied for the detection of mercaptan in ether, in case such an impurity is suspected, which is unlikely, see Berthelot, *Compt. rend.*, **108**, 350.

ether for some time, mercury may be obtained as a gray powder, which consists of minute globules of the metal; this powder is slowly oxidized on contact with the air, especially in the presence of moisture, and the powder, whether metallic or oxidized, might be readily confused with that described as resulting from agitating ether containing sulphur or sulphur compounds with pure mercury.

III. (a) DETECTION OF WATER AND ALCOHOL IN ETHYL ETHER.

In the first decade of the modern chemical period chemists generally only busied themselves with removing from freshly distilled ether any acids or "oil of wine" formed during the manufacture, and little attention appears to have been given to the removal of all the water and alcohol present in ether prepared according to the methods then employed. However, there would have been no object for such a procedure on any large scale, since ether was employed principally in the form of "Liquor anodynus Hoffmani" as a medicinal preparation; and the presence of such amounts of water and alcohol as probably occurred in the ether of that day would not have interfered with any of its limited applications. Moreover, it is doubtful if the chemist of 1800 could possibly have produced a purer ether than was obtained by the methods of Woulfe, Pelletier, and Scheele, together with subsequent fractionation. The grade of ether obtained at that time by the most refined methods at the disposal of the chemists—their rectified ether—possessed a specific gravity of 0.758, which shows that it contained considerable amounts of water and alcohol. In 1816, however, Guy-Lussac obtained an ether possessing a density of 0.7214 at 15°/4° by washing commercial ether with water and treating the product with lime.

About 1836, potassium carbonate began to be used as a dehydrating agent for ether, it serving also to remove any acids present, and alcohol was removed in part by rectification. Later (about 1845) it was learned that ordinary crude ether might be freed from water and alcohol either by placing it in contact with fused calcium chloride, or by agitating it repeatedly with two parts of water, separating the upper layer of liquid, then drying over quicklime or calcium chloride and rectifying carefully. By using such methods of purification ether possessing a specific gravity of 1.718 at 15°/4° was obtained, which shows that the product was one of considerable purity. Still later (1865), it was considered that pure ether possessed a specific gravity of 0.735–0.736 at 0°/4° (0.718–0.719 at 15°/4° C.). Making allowance for the less refined methods of determining this constant in use then, it may be said that it was possible to prepare ether quite free from water and alcohol.

TESTS FOR THE DETECTION OF WATER IN ETHER.

The tests which have been proposed for the detection of moisture in ethyl ether are quite numerous and many are so lacking in delicacy that they scarcely merit any consideration at all. These tests have all been dependent upon the deportment of water with

the reagent employed, and consequently may be conveniently classified as follows:¹

I. THOSE TESTS BASED UPON THE COLOR ASSUMED BY THE HYDRATION OF A DEHYDRATED COMPOUND.

1. *The Test with Anhydrous Copper Sulphate.*—Copper sulphate rapidly absorbs water, forming the mono- or the pentahydrate. These facts induced Adrian² to recommend the use of the salt as a test for the presence of moisture in ether, and this test is quite generally recommended and employed. It is usually directed that one gram of anhydrous cupric sulphate be shaken with 20 cc. of the ether under examination, and mere traces of water may be thus detected. The presence of alcohol does not interfere, since absolute alcohol forms no compound with anhydrous cupric sulphate under the conditions which obtain. Cupric sulphate is insoluble in absolute alcohol and ethyl alcohol is much less active than methyl alcohol in promoting the decomposition of cupric sulphate.

2. *The Test with Cobalt Chloride.*—Winkler³ showed that anhydrous cobalt chloride undergoes a change in color from blue to red in the presence of water; and Napier⁴ suggested that this reaction may be applied for the detection of water in ether. He recommended that paper colored with a solution of the salt be employed, a change in color indicating the presence of water. Alcohol in no way interferes with this test, but it is much less delicate than cupric sulphate, even when anhydrous cobalt chloride is used. We have prepared several samples of ether which gave a positive result with anhydrous cupric sulphate and failed to respond for moisture when anhydrous cobalt chloride was used.

3. *The Molybdic Acid Test.*—Mann⁵ proposed the following test: When an aqueous solution of two parts of crystalline citric acid is mixed with one part of molybdic acid and the mixture is then evaporated to incipient fusion in a porcelain capsule, the deep blue mass which is formed, if heated with 30 to 40 parts of water and filtered, yields along with a fixed residue a faint yellowish brown filtrate, holding in solution a compound which possesses the property of appearing deep blue in its anhydrous state, but almost colorless when hydrated. When filter paper is steeped in this solution and then dried at 100°, the blue color appears with great intensity and the presence of water in ether may be detected by plunging the paper into the sample under examination.

This test is even less delicate than the preceding one, being reliable only in the presence of considerable amounts of water.

4. *The Thiocyanic Acid Test.*—Parenti⁶ found that by the action of thiocyanic acid on filter paper a rose color is produced which is not altered by anhydrous

¹ The tests will be considered in the order of their importance.

² *Mon. Sci.*, **44**, ii, 835.

³ *J. prakt. Chem.*, **91**, 209; see also Franz, *Ibid.*, [iii] **5**, 274. On the Hydrates Formed by Cobalt Chloride with Water, see Potilitzin, *Ber.*, **17**, 276.

⁴ *Bull. soc. chim.*, **29**, 122.

⁵ *Chem.-Ztg.*, **4**, No. 19; *Archiv. Pharm.*, [3], **17**, 122. On the deportment of molybdenum trioxide with citric acid, see Henderson, Orr, and Whitehead, *Trans. Chem. Soc.*, **75**, 546.

⁶ *Gazz. chim. ital.*, **19**, 175.

ether, whereas ether containing water produces a brilliant green stain in the colored paper. This color is discernible only after the evaporation of an ether containing considerable amounts of water.

5. Strömholm¹ has found that *mercuric chloride and water* combine as hydrate in an ethereal solution. This reaction, however, does not suffice to detect minute amounts of water in ether.

II. THOSE TESTS BASED UPON DEHYDRATION.

Regnauld and Adrian² recommended that the presence of water in ether be determined by ascertaining the density of the ether before and after the action of pure, dry potassium carbonate. This test is of interest historically—it was announced in 1864—but is inconvenient, owing to the fact that the temperature should be kept at 15° and because prolonged agitation with the potassium carbonate is necessary, and it has not been employed for these reasons.

III. TESTS DEPENDENT UPON REDUCTION.

Claus³ found that if some crystals of sublimed "hydro-anthraquinone" are treated with pure ether, they are converted into brownish black crystals; however, water produces a magnificent red coloration which disappears on contact with air but which reappears on standing. Squibb⁴ found that "hydro-anthraquinone" is even more sensitive to water than anhydrous cupric sulphate.

This test appeared so promising that it was decided to investigate it carefully, in order to determine its accuracy and delicacy for detecting minute amounts of moisture in ether. On the addition of several milligrams of anthraquinone and a small piece of 2 per cent. sodium amalgam to pure ether, and after thorough agitation, it was found that a pronounced red oily separate formed in the presence of water and that the amalgam assumed a red tint. In the presence of alcohol, however, the amalgam becomes green in color. Therefore, it was thought that anthraquinone and sodium amalgam could be employed for the detection of both of these impurities of ether.

To 50 cc. of pure ether, several milligrams of anthraquinone and a small quantity of sodium amalgam were added, and the mixture was then well shaken. The sodium amalgam was unaffected, but on the addition of 0.85 cc. of absolute ethyl alcohol it assumed a green color when the mixture was shaken; and it was found that 1.5 to 2.0 per cent. of alcohol might be readily detected in ether by this method. In applying this test for the detection of alcohol, after the addition of the reagents, the mixture should be shaken well and then allowed to stand for at least one hour.

The addition of 0.05 cc. of water to the above-mentioned ether containing alcohol resulted in the formation of a slight red-colored separate, which disappeared immediately upon shaking the mixture. The addition of 0.1 cc. of water produced a more marked separate, which possessed greater permanency. With 0.6 cc. of water the amalgam decomposed

wholly and the red-colored substance reappeared on standing. It was thus found to be possible to detect 0.1 per cent. of moisture in ether by this method, since the red substance forms around the amalgam and is easy to discern.

The addition of 0.05 cc. of water resulted in the formation of the red-colored separate in 50 cc. of ether, using the same amounts of reagents as before; but this separate disappeared on standing, the amalgam became dark colored, and there was no recurrence of the color after the mixture had been allowed to stand 30 minutes. The presence of 0.2 per cent. of water in ether gave a much more marked reaction, and the colored separate afforded by ether containing 0.3 per cent. of moisture is quite permanent. In fact, the permanency of the color depends entirely on the extent to which the amalgam is decomposed.

Considerable care is necessary in applying this test, since, when mere traces of impurity are present, the colors are not permanent and are difficult to recognize, and must therefore be carefully observed. Since sodium amalgam is decomposed by water, an excess of the amalgam is necessary to secure the green color, which is produced only when alcohol is present. This test for alcohol is only satisfactory when water is present in traces.

IV. TESTS BASED UPON THE EVOLUTION OF GAS.

1. *The Test with Sodium.*—This is usually given as follows: When 15 cc. of the ether are put into a perfectly dry test tube and a piece of metallic sodium about 5 mm. in diameter is added, there should result only a very slight evolution of gas, and the sodium should possess, even after standing six hours, a distinct metallic luster. In a sample of ether not previously treated with sodium or in a sample not distilled over the metal, the latter becomes coated with white sodium hydroxide, more or less colored by the presence of acetaldehyde, during the progress of the test.

This test could be referred to more appropriately as a test for acetaldehyde and water, since in the presence of the former the sodium possesses, at the expiration of the test, a yellow or orange coating, and when acetaldehyde is treated with sodium, hydrogen is liberated. In the case of the ethers examined by the authors, only those distilled over sodium complied with the test; and although the sodium possessed a distinct metallic luster after six hours, the evolution of gas continued for over an hour.

The above test with sodium may be used in the examination of anaesthetic ether, in which case the latter should be colorless at the end of six hours; there should be no separation of a flocculent precipitate of sodium hydroxide or of a form inducing turbidity, and the coating on the sodium should be white and of limited amount.

2. *The Test with Sodium Dioxide.*—Sodium dioxide, obtainable in a convenient compact form commercially as "oxone," may be used instead of sodium in testing anaesthetic ethers, in which instance but a slight evolution of gas should result. In the presence of more than traces of moisture, we have ob-

¹ *Z. physik. Chem.*, **44**, 63.

² *Bull. soc. chim.*, **6**, 461.

³ *Ber.*, **10**, 927; see also Leeds, *J. Am. Chem. Soc.*, **1**, 38.

⁴ *J. Am. Chem. Soc.*, **1**, 38.

served a reddish separate, the composition of which was not determined.

3. *The Test with Calcium Carbide.*—Vitali¹ found that water in ether may be detected by treating with calcium carbide and passing any acetylene evolved into an ammoniacal silver nitrate solution. This test was applied to the ethers which gave a positive reaction with sodium by adding one gram of crystalline calcium carbide to 20 cc. of the sample, and in every case acetylene in sufficient amounts to be readily recognized was evolved.

Since one gram of water yields, at 0° C. and 760 mm., 580 cc. of acetylene, water in ether, when present in considerable amounts, may be estimated by passing the acetylene evolved from allowing an excess of powdered calcium carbide to fall into a fixed quantity of the ether, into a saturated salt solution, also saturated with ether and acetylene, contained in a vessel furnished with an outlet tube, through which the volume of salt solution displaced by the gas passes into a suitably graduated vessel.² It is necessary to keep the apparatus at a constant low temperature during this estimation.

V. TESTS DEPENDENT UPON THE LAW OF PARTITION.

1. *The Potassium Phenolate Test.*—Romei³ found that the extremely hygroscopic substance, dry potassium phenolate, is quite insoluble in anhydrous ether, but that it partly dissolves in that liquid when it contains water, imparting to it a reddish brown color. When this test is carefully conducted, it is delicate enough to detect 0.25 per cent. of water in ether, oily drops of a brownish color separating and the ether becoming turbid; but it lacks the delicacy necessary for detecting mere traces of moisture.

Hewitt⁴ states that the presence of water may be detected in ether by means of "potassium phosphate," which is insoluble in anhydrous ether, but dissolves partially in ether containing water, a brown residue being left. He undoubtedly refers to potassium phenolate.

2. *The Picric Acid Test.*—Bougault⁵ proposed a test for the detection of water in ether which is dependent on the color of the aqueous solution of picric acid. A saturated solution of picric acid in anhydrous ether is devoid of color; but on the addition of a trace of water the usual deep color develops. At a specific gravity of 0.725 the intensity of the coloration appears to attain a maximum, and Bougault considered that it is possible to utilize this fact as basis of a test for the presence of moisture in ether. Since even a 0.01 per cent. solution of picric acid in water is distinctly yellow,⁶ this test may be used between the limits of density 0.720 to 0.725 as a test for the amount of water present in commercial ether, but it is lacking in delicacy.

3. *The Test with Tannin.*—Luboldt¹ proposed that on shaking the ether with dry tannin, the latter must not liquefy but remain in the form of a powder. Since, however, tannin will also deliquesce to a sirup if a small proportion of alcohol is present, this test is not suitable for detecting moisture in ether. Nevertheless, it is sometimes recommended for the purpose.²

VI. TESTS DEPENDENT UPON DECOMPOSITION.

These tests are, in general, based upon the decomposition of a double salt by water.

1. *The Test with the Double Iodide of Lead and Potassium.*—Brooks³ found that the double iodide of lead and potassium, $\text{PbI}_2 \cdot 2\text{KI}$, is decomposed by water, which property, since it results in the formation of lead iodide and potassium iodide, he considered, renders this salt a delicate test for the presence of moisture in ether. In fact, he regarded it as more delicate than the test with anhydrous cupric sulphate, and this is undoubtedly true. However, the presence of peroxides⁴ in the ether under examination would interfere somewhat with this test. Furthermore, E. C. McKelvy, of the Bureau of Standards (private communication), has found that the test for water with the double iodide and potassium is interfered with by alcohol. He found that potassium iodide is soluble in absolute alcohol at 30° to the extent of approximately 2 per cent.

2. *The Test with the Double Iodide of Lead and Ammonium.*—A similar test to the preceding was proposed by Mosnier,⁵ who found that the double iodide of lead and ammonium, $3\text{PbI}_2 \cdot 4\text{NH}_4\text{I}$, is unaffected by pure ether, but is decomposed in the presence of moisture.

VII. TESTS DEPENDENT UPON THE PRODUCTION OF A TURBIDITY.

Not a few tests belonging to this class have been proposed, but all of these are deficient in delicacy and are comparatively valueless. They are given to make the paper complete.

1. *The test with carbon disulphide* is the best known of this class and is usually applied by mixing the ether with an equal portion of carbon disulphide, after which there should result no turbidity.⁶ Böttger⁷ recommended adding potassium hydroxide to the ether-carbon disulphide mixture in order to ascertain whether the turbidity is due to the presence of water or alcohol; carbon disulphide is miscible in all proportions with alcohol and ether, however, so this test is unnecessary.⁸ In the presence of considera-

¹ *J. prakt. Chem.*, **77**, 357. "On the Solubility of Tannin in Absolute Ether," see Bolley, *Ann.*, **115**, 63; *Chem. News*, **2**, 270.

² For instance, by Classen ("Handbuch der Qualitativen Chemischen Analyse," **1906**, p. 301).

³ *Chem. News*, **77**, 191; see also *Pharm. Centralk.*, **39**, 509. Biltz (*Ber.*, **40**, 2182) has found that potassium lead iodide, which is almost colorless, is decomposed by water with the formation of lead iodide and has suggested it as a reagent for moisture.

⁴ The department of peroxides with various iodides will be discussed later.

⁵ *Ann. chim. phys.*, **12**, 382.

⁶ Beilstein ("Handbuch der Organische Chemie," **1**, 294). This test is given in the British and Mexican Pharmacopoeias.

⁷ *Polyt. Notizblatt*, **17**, 288.

⁸ Tuchschildt and Follenius, *Ber.*, **4**, 583.

¹ *Boll. chim. farm.*, **37**, 257; see also Yvon, *Z. anal. Chem.*, **28**, 448.

² Water may be determined in petroleum by a similar method. See *Met. and Chem. Eng.*, **8**, 283. Cf. also Masson, *Chem. News*, **103**, 37.

³ *Z. anal. Chem.*, **8**, 390.

⁴ "Anaesthetics and Their Administration," **1907**, p. 22.

⁵ *J. Pharm. Chim.*, [6], **18**, 116.

⁶ "On the Solubility of Picric Acid in Water," see Marchand, *J. prakt. Chem.*, **64**, 91; and Findlay, *Trans. Chem. Soc.*, **81**, 1219.

ble amounts of water,¹ however, a marked turbidity results when an equal volume of carbon disulphide is mixed with the ether under examination. This test has met with great favor, especially in Great Britain.

2. *The Test with Oil of Copaiba*.—Blanchet² recommended that when ether is mixed with an equal volume of oil of copaiba there should result no turbidity. Squibb³ obtained an ether which did not show the faintest cloudiness with either carbon disulphide or oil of copaiba when previously mixed with 0.1 per cent. of alcohol containing water; and oil of copaiba forms an emulsion if added to an ether containing alcohol. Hence the test is never employed for the detection of water in cases in which accuracy is desirable.

3. *The Test with Oil of Laurel*.—Hancock⁴ found that equal volumes of oil of laurel and pure ether gave no turbidity when mixed, but when water was added a pronounced cloudiness resulted. Alcohol will also cause a turbidity. The test is of less value than the preceding.

4. *The Test with Oil of Turpentine*.—Proctor stated that pure ether forms a clear solution with oil of turpentine in all proportions, whereas ether containing water produces a milky mixture, which, after standing some time, becomes clear from the deposition of the separated water. The test is of no value.

5. *The Test with Benzol*.—Grier,⁵ who employed carbon disulphide and benzol for the detection of water in ether, found that carbon disulphide is the more delicate reagent, giving a turbidity with samples of ether which remained perfectly clear with benzol. The test is valueless.

6. *The Test with Liquid Paraffin*.—Crismer⁷ found that liquid paraffin (b. p. = 215°–240° *in vacuo* at 6 mm. pressure) mixes with ether, when it is freed from water and other impurities by means of sodium, in all proportions, and gives a clear solution; but that the presence of water or water containing alcohol renders this solution turbid. This test is of little value.

There are several other tests which have been proposed for the detection of traces of water in gases, etc.,⁸ which could be applied for the detection of moisture in ether; but these are lacking in delicacy and, as a rule, are not applicable in the presence of all the other impurities.

(b) *The Dehydration of Ether*.—Among the substances which have been recommended for the drying of ether are the following: Anhydrous sodium sulphate, calcium chloride, potassium carbonate, magnesium sulphate, sylvine, potassium chloride, calcium sulphate, and carnallite. Of these, it has been found that calcium chloride and potassium carbonate are efficient drying agents, and that sodium sulphate

dries ether but slowly. Von Siebenrock¹ has found that sodium sulphate may be advantageously replaced by carnallite or magnesium sulphate, when the ether contains easily saponifiable impurities.

Calcium oxide and freshly prepared fused potassium hydroxide have also been employed for drying ether, which remains unaltered when kept over either substance, just as when it is stored over potassium carbonate.

It is usual in preparing pure ether to remove the water and alcohol in one operation by shaking the ether several times with one-half its volume of water, separating and drying over calcium chloride for several hours,² and then distilling. Lieben,³ however, recommended shaking with 20 to 30 separate small quantities of water, and then redistilling over sodium or phosphorus pentoxide. Ether distilled over sodium, when kept in well-stoppered bottles, remains pure for several months and little alteration occurs even in much longer periods.⁴

Purification by means of sodium is sufficient to remove all impurities objectionable in ether intended for anaesthetic purposes. An ether containing moisture and small amounts of other impurities may be readily purified by adding ten grams of sodium wire to a liter in a flask provided with a calcium chloride tube, and then allowing the mixture to stand for three or four days in a cool place, after which it is filtered. The ether thus prepared may be kept over sodium. It must be filtered at the time of use.⁵

Wislicenus and Kaufman⁶ found that amalgamated aluminium has no action on anhydrous ether, but that traces of water, if present, are at once attacked with liberation of hydrogen; hence they suggested its use in rendering ether anhydrous. Amalgamated aluminum is safer to handle than sodium or sodium-potassium alloy. It may also be used as a reagent for the detection of moisture in ether, and, from our experience, is very delicate.

Other methods may be used for preparing anhydrous ether on a small scale; these are either dependent upon the employment of dehydrating agents already mentioned or are based upon the use of a substance which removes other contaminants and impurities at the same time. Methods of the latter class will be referred to when the other impurities are discussed; and it is only necessary to refer here to the use of calcium carbide for such a purpose.

Yvon⁷ found that absolute alcohol could be prepared from alcohol of 95 per cent. strength, by adding a quarter of its weight of calcium carbide in coarse powder, agitating at intervals for two hours, and then allowing the mixture to rest for twelve hours. It is then distilled and a little anhydrous copper sul-

¹ *Monatsh.*, **30**, 759.

² Ether should not be kept over calcium chloride, since pure ether undergoes alteration when kept with calcium chloride in well stoppered bottles for lengthy periods. Sodium chloride and copper sulphate also induce alteration (Lieben).

³ *Ann. Suppl.*, **7**, 218. See also Mendeléeff *Ann.*, **119**, 1; and Oudemans, *Rec. trav. chim.*, **4**, 269.

⁴ Cf. Lieben, *Chem. News*, **27**, 43.

⁵ Modification of Stolle's method (*J. Pharm. Chim.*, **27**, 105).

⁶ *Ber.*, **28**, 1323.

⁷ *Compt. rend.*, **125**, 1181.

¹ Water dissolves about 1/1000th of its weight of carbon disulphide (Sestini, *Gazz. chim. ital.*, **1**, 473).

² *Ann.*, **7**, 157.

³ *Chem. News*, **51**, 69.

⁴ *Edinb. Phil. J.*, **1830**, 50.

⁵ "Pharmaceutical Testing," **1890**, p. 43.

⁶ *Pharm. J.*, [iv], **6**, 293.

⁷ *Ber.*, **17**, i, 649 (1884).

⁸ For example, the ferrous ammonium sulphate-potassium ferri-anide test of Scriba (*Z. phys. chem. Unterr.*, **19**, 298).

phate is added to the distillate, which is redistilled from the copper acetylide formed. However, the product obtained by this method possesses an unpleasant odor and taste.¹ Vitali² recommended using mercuric nitrate to remove the unpleasant odor, then filtering and distilling over dry potassium carbonate. He found that an absolute product could thus be obtained and that it had no foreign color. Dehydration by means of metallic sodium is less expensive.

(c) *Tests for the Detection of Alcohol in Ether.*—Although it has been maintained by some that ether used for anaesthesia should be free from alcohol as well as water,³ and ether containing small amounts of alcohol has sometimes been regarded as "adulterated,"⁴ yet, as indicated previously, the addition of alcohol to ether in amounts up to 4.00 per cent. does not interfere with the employment of the ether for anaesthetic purposes and this amount is allowed by some pharmacopoeias; furthermore, some manufacturers assert that alcohol exerts a preserving action on ether.

It is often desirable, however, that ether intended for certain chemical work should be free from alcohol, and in such cases it is necessary to test for its presence; in other cases it is important that the amount of alcohol present does not exceed a certain specified limit, and then it is necessary to determine the amount present. With the object of finding just what tests and methods of estimation are suitable and reliable, all of the schemes for the detection and determination of alcohol in ether were studied, and where the method appeared worthy it was tried out. For convenience sake, these methods will be considered in classes, an arrangement based upon the reactions which occur when the alcohol reagent is applied.⁵

1. COLORIMETRIC TESTS DEPENDENT UPON A MIXTURE OF SOLVENTS.

1. *The Rosaniline Acetate Test.*⁶—This undoubtedly delicate test may be applied as follows: A minute quantity of powdered rosaniline acetate, previously dried at 100°, is placed in a dry test tube, 10 cc. of the ether are added, and the tube is corked and well shaken. No amethystine color is imparted to the ether when it is pure and anhydrous, but when alcohol or water is present the coloration is more or less intense. This test is recognized by the Pharmacopoeias of Mexico, Spain and France.

When an ether which gives a response to this test is well shaken with anhydrous calcium chloride, in order to remove alcohol and water, it no longer possesses the ability to dissolve rosaniline acetate, becoming only very faintly tinged when agitated with the salt.

¹ See Ostermayer, *Pharm. Ztg.*, **43**, 99.

² *Boll. chim. farm.*, **37**, 257.

³ In this connection, see Howard, *Lancet*, **1875**, ii, 228.

⁴ For a case in point, see Baird, *Proc. Mass. Pharm. Assn.*, **1906**, 58.

⁵ Two samples out of three examined were found to be "adulterated."

⁶ On the Estimation of Ethyl Ether in Alcohol, see Wolff, *Chem.-Ztg.*, **34**, 1193. This method serves for the approximate estimation of ether in alcoholic solution; the results obtainable are a trifle low.

⁷ Pratesi (*Le Technol.*, **1875**, No. 415; *Am. Chemist*, **6**, 196) suggested the use of "aniline red" as a test for alcohol in ether.

Allen⁷ operated in this manner: A minute quantity of powdered fuchsine is placed in a narrow test tube, 10 cc. of the ether are added, the tube is corked, and the whole is shaken. If the coloration is considerable, 10 cc. of ether which has been treated with calcium chloride are placed in another tube of the same bore as the first, and fuchsine is added as before. Alcohol is then added from a calibrated burette in 0.1 cc. lots, shaking after each addition until the liquids possess the same depth of color. It is well to allow the alcohol to drop right into the ether, and not allow it to run down the sides of the tube, since in the latter case it will dissolve any adherent particles of fuchsine, forming a solution which will be precipitated on mixing with the ether. For a similar reason, it is not convenient to dilute the sample with pure ether, so as to reduce the color to that of a standard tint. In practice, each 0.1 cc. of alcohol added from the burette may be considered as indicating 1 per cent. of impurity in the sample, and the results are accurate within 0.25 per cent. Sometimes the tints of the two liquids are not readily comparable, but on placing the tubes in cold water for several minutes, this difficulty is overcome.

This method is suitable for approximately determining small amounts of alcohol, but it is difficult to apply when the alcohol exceeds 5 per cent. Increasing proportions of nearly water-free alcohol up to about 0.2 per cent. may be added to a nearly water-free ether without increasing the depth of the tint. When it is carefully applied, fuchsine is a very sensitive test for the presence of water,⁸ but it is less delicate for detecting alcohol. In applying the method, only minute amounts of fuchsine are used and it is necessary that equal amounts be weighed into both the ether under examination and the standard;⁹ otherwise only approximate results are obtained. As a rule, high results are obtained.

The following results were obtained with various anaesthetic ethers, employing anhydrous ether as a standard:

Ether No.	Impurity by absolute alcohol. Per cent.	By 95 per cent. alcohol. Per cent.
1.....	...	5.0
2.....	...	6.0
3.....	...	5.5
7.....	1.0	1.5
8.....	7.0	6.5
9.....	5.5	6.0
10.....	6.0	6.0

In the presence of water, the occurrence of alcohol in an ether may be ascertained with the fuchsine method by drying a portion of the sample over anhydrous potassium carbonate or calcium carbide, and then testing a 10 cc. portion as directed above.

We are of the opinion that *rosaniline tannate*,⁴ which is insoluble in water but soluble in alcohol, may be employed as a test for the detection of the

¹ *Analyst*, **2**, 97.

² Squibb, *Chem. News*, **51**, 76.

³ When varied amounts of fuchsine are added to portions of an ether containing 3 per cent. of alcohol and a small amount of water, different depths of color result.

⁴ See Kopp, *Jahresber.*, **1862**, 694

latter, or for determining whether the red coloration obtained with fuchsine is due to the presence of moisture or alcohol.

2. *The Aniline Violet Test.*—Stefanelli¹ recommended that when ether is shaken with a little aniline violet, no coloration should result. He found that the ether becomes colored even in the presence of a minute quantity of alcohol, but, according to others,² it would appear that 1 per cent. of alcohol is the minimum amount which may be definitely recognized by this test. Rosaniline acetate is preferable to mauveine.

3. *The Test with Jalap Resin.*—Reghini d'Olleggio³ found that when jalap resin is added to ether containing alcohol, and the mixture is agitated, a decided coloration results. This test is of no real value, however, since jalap resin will not readily dissolve in ether unless it contains some 15 per cent. of alcohol.

4. *The Test with Anthraquinone and Sodium Amalgam.*—As mentioned under the tests for water, anthraquinone and sodium amalgam may be used for the detection of alcohol. When water is present, the ether should be dried over anhydrous potassium carbonate or calcium carbide, before applying this test for the detection of alcohol.

5. *The Test with Cobalt Chloride and Potassium Thiocyanate.*—Grassini⁴ found that when a dilute solution of cobalt chloride, the concentration of which is not less than 0.5 per cent. and is best about 5 per cent., is mixed with potassium thiocyanate solution and a layer of alcohol is poured on the liquid, which is then shaken gently so that the two strata do not mix, the alcohol assumes an azure-blue color, which is most intense at the line of contact. If ether is used in place of alcohol, no coloration is obtained, so that Grassini concluded that the reaction may be used as a means of detecting the presence of alcohol in ether. Since, however, the coloration is destroyed by peroxides and no marked coloration results unless about 5 per cent. of alcohol is present in an unoxidized ether, it is of little, if any, value.

II. TESTS DEPENDENT UPON DECOMPOSITION.

These tests are, in general, quite accurate, if properly conducted, but are not characteristic of alcohol alone.

1. *The Iodoform Test.*—The test of Lieben, as modified by Hager,⁵ is as follows: To 10 cc. of the ether, 5 or 6 drops of a 10 per cent. solution of sodium or potassium hydroxide are added, and the liquid is warmed to about 50°. A solution of potassium iodide, fully saturated with free iodine, is next added drop by drop with agitation, until the liquid becomes permanently yellowish brown, when it is carefully decolorized by a further cautious addition of the caustic alkali solution. If alcohol is present, iodoform is gradually deposited at the bottom of the tube in yellow

low crystals, which, after standing, may be examined with a lens. Under a microscopic power of 300 diameters, the appearance of the deposit is very characteristic, the usual crystal forms being hexagonal plates, stars, and rosettes.

This test is not peculiar to alcohol, however, iodoform being produced by acetone, acetaldehyde, isopropyl, propylic and butylic alcohols and aldehydes, various ethers, meconic, laevulic and lactic acids, turpentine, sugar, etc. Since acetaldehyde is the only one of these substances which is likely to occur in ether of other than the commercial grade, the ether should always be examined for this very common contaminant before applying the iodoform test for the detection of alcohol.

Very careful purification is necessary to obtain ether which does not respond to the test of Lieben,⁶ and mere keeping in the presence of moisture generates traces of impurities sufficient to produce the reaction. This has been clearly demonstrated by Lieben.⁷

Classen⁸ has suggested that the ether be agitated with water, and that the aqueous extract be then tested for alcohol by means of Lieben's method; and we have found that this may be more satisfactorily applied by shaking 30 cc. of the ether under examination with 20 cc. of water, warming to 40° to expel any dissolved substances other than alcohol, and then applying Lieben's test as modified by Hager. In this manner, if only slight traces of acetaldehyde are present, a positive result is indicative of the presence of alcohol when anaesthetic ether is being examined.

2. *The Method of Estimation by Means of Potassium Dichromate.*—Nicloux⁴ has found that water at 40° absorbs the whole of ethyl alcohol in the state of vapor and but a trace of ether, thereby permitting of a quantitative method of separation. The ether to be examined is placed in a flask, which serves as a generator for the vapor. The latter is passed through seven flasks, the first three of which, each containing 20 cc. of water, are placed in a vessel of water at 40° C. and the last four, each containing 20 cc. of 50 per cent. sulphuric acid, are at room temperature. The temperature in the generator is very gradually raised to 80°–90° C. and the vapor is aspirated through the absorbing vessels. The ether absorbed by the sulphuric acid may be determined by the dichromate method.⁵ It is more satisfactory, however, to de-

¹ Concerning this test, see Vulpius, *Pharm. Centralk.*, **14**, 117, and Adrian, *Mon. sci.*, **44**, ii, 835.

² *Chem. News*, **27**, 43. Lieben pointed out that when ether and water are heated to 100°, alcohol is formed in a short time. The same reaction, he found, obtains at the ordinary temperature, but only after the lapse of a considerable time; ether kept with water in well-stoppered bottles was found to exhibit the iodoform reaction after some three or four months, but in some instances the reaction was obtained in a shorter time. It will appear later, when the oxidation of ether is discussed, that the samples of ether which exhibited the iodoform reaction under the conditions described by Lieben contained acetaldehyde, which is formed by the slow oxidation of ether in the presence of moisture. It is of interest to mention here, however, that Erlenmeyer, Darmstadter, and Tscheppé (*Z. Chem.*, **4**, 341) have found that on heating ether with water, to which has been added a small amount of sulphuric acid, for some time to 150°–180°, ethyl alcohol is formed.

³ "Handbuch der Qualitativen Chemischen Analyse," **1906**, p. 302.

⁴ *Compt. rend. soc. biol.*, **61**, 665.

⁵ *Ibid.*, **61**, 577, 606.

¹ *Ber.*, **8**, 439; *Le Technol.*, **1875**, No. 415.

² For example, the *National Standard Dispensatory*, **1905**, p. 111.

³ *Le Technol.*, **1875**, No. 415.

⁴ *L'Orosi*, **23**, 224, 297; *Z. allgem. Oesterr. Apoth.*, **55**, 837.

⁵ *Z. anal. Chem.*, **9**, 492; Hager's "Handbuch der Pharm. Praxis," **1**, 167 (1876); Allen's "Commercial Organic Analysis," **1**, 90.

termine the alcohol which is absorbed by the water in the vessels heated to 40° C.

It is important to note that Nicloux did not suggest this method as one suitable for determining alcohol in ether, but only as a general method for the quantitative separation and simultaneous determination of small quantities of ether and alcohol. It is, however, entirely suitable for the purpose, particularly when large amounts of alcohol are present in ether; and the approximate amount of alcohol may be determined by this method, quite rapidly, as follows:

Ten cc. of the ether are thoroughly agitated with 40 cc. of water and the aqueous extract is then warmed to 40° C. to expel any dissolved ether. The alcohol is then determined by titration with potassium dichromate solution (19 grams to one liter) in the presence of sulphuric acid, the end point of the reaction being detected by the change of color of the solution from bluish green to yellowish green.¹

3. *The Method of Detection Based upon the Oxidation to Aldehyde.*—Lassar-Cohn² proposed the following test for the detection of alcohol in ether: The ether is shaken with water, the aqueous layer is removed and freed from dissolved ether by careful warming, and the alcohol remaining in the water is oxidized by means of manganese dioxide and sulphuric acid; the aldehyde produced is then distilled off, and the distillate may be tested with Nessler's reagent.

This method, as originally proposed, is almost totally defective, owing to the fact that alcohol itself gives a reaction with Nessler's solution. It is, therefore, better to proceed as follows: Agitate 10 cc. of the ether with 40 cc. of water in a ground glass-stoppered bottle, and the aqueous layer, which will show an increase in volume greater than 10 per cent. of the ether taken, depending on the amount of alcohol present, is removed and then freed from dissolved ether by careful warming at 40° C. for about an hour. The alcohol in the water is then oxidized by means of potassium dichromate and sulphuric acid, the aldehyde produced is distilled off, and the approximate amount contained in the distillate is determined colorimetrically by the method of Francois.³

4. *The Method of Estimation Based upon the Production of Acetic Acid.*—Freyer⁴ has proposed a method for the detection and estimation of alcohol in ether, which, although we have not had occasion to use it, cannot be recommended on account of its doubtful accuracy and comparative cumbrousness. Accord-

¹ This method is based upon one proposed by Nicloux (*Bull. soc. chim.*, 35, 330) for the determination of alcohol in chloroform.

² *Z. anal. Chem.*, 33, 251. An analogous method is the process of Denigès (*Bull. soc. chim.*, 7, iv, 951) for the detection of ethyl alcohol in the presence of methyl alcohol; this depends on the fact that bromine water has but little oxidizing action on warm methyl alcohol, whereas it converts ethyl alcohol on warming into acetaldehyde. Similar also is the test devised by Kossa (*Pharm. Centralh.*, 46, 893), who found that if 90 per cent. ethyl alcohol is carefully poured on to an equal amount of 50 per cent. nitric acid so that two layers are formed, a white cloudy layer appears at the surface of contact after a few minutes, and soon afterwards a green or bluish green ring is observed on the lower side of this. The green layer sinks gradually, effervescence occurs, and acetaldehyde is formed. Kossa, therefore, suggested this behavior as a sensitive test for the presence of ethyl alcohol. Acetaldehyde, ethyl ether, acetone, and chloroform do not give the reaction.

³ See tests for the detection of acetaldehyde.

⁴ *Z. landw. Versuchs-Wes. Oesterr.*, 4, 955.

ing to this method, the amount of alcohol and water is estimated by agitating 20 cc. of the sample with a saturated solution of calcium chloride and noticing the diminution in volume. 25 cc. of the sample (which, if it contains more than one gram of alcohol and water, should be diluted with anhydrous ether) are then put into an Erlenmeyer flask, mixed with 50 cc. of a ten per cent. solution of acetyl chloride in chloroform, and the flask is closed with an India rubber stopper, through which passes a separating funnel containing 100 cc. of water. After the lapse of an hour, a little of the water is introduced, and the whole is well shaken and then titrated with 2 N alkali, phenolphthalein being used as an indicator. A blank experiment is then made with 50 cc. of the acetyl chloride solution, mixed with anhydrous ether, which is titrated in the same manner. The difference in the two titrations represents the alcohol, inasmuch as by the action of alcohol on acetyl chloride only one mol. of free acid is formed, while water liberates 2 mols. One cc. of 2 N alkali equals 0.092 gram of 1.1157 cc. of alcohol.

This method is based on the well known reaction which occurs when acetyl chloride is heated with any substance containing the radical hydroxyl, but apparently no consideration was given to the formation of acetoxyl by the action of acetyl chloride on alcohol.

III. TESTS DEPENDENT UPON SOLUBILITY, OTHER THAN COLORIMETRIC TESTS.

1. *The Test Based upon Contraction in Volume.*—

A test which is indicative of the absence of an undue amount of alcohol or water in ether is that based upon the solubility of pure ether in water.¹ This test is specified by the Pharmacopoeia of the United States (1905, p. 31) as follows: When 20 cc. of ether are shaken with 20 cc. of water in a graduated tube, the water being just previously saturated with ether, the ether layer, upon separation, should measure no less than 19.2 cc.

Although agitation with water extracts most of the alcohol ether may contain, yet, according to the law of partition, it does not appear that a quantitative method may be based upon this, especially when much alcohol is present. Allen² follows this procedure: A small quantity of fuchsine is placed in a separator or Mohr's burette, which is then filled with water and a small proportion of ether, and the whole is agitated. By this means, a colored etherized water is obtained, in which ether is quite insoluble, while alcohol readily dissolves. Ten cc. measure of the etherized water is run into a glass tube holding about 25 cc., and having divisions of 1/10 cc.; 10 cc. of the sample of ether are then next added, the tube is corked, and the whole is well shaken. On the ether rising to the surface, its volume can readily be read off. Any reduction in its volume is due to admixture of alcohol. Thus each 0.1 cc. lost represents 1 per

¹ It is generally stated that a good ether must not dissolve in water to the extent of more than 10 per cent. On the contraction of ether by agitation with water, see Muscis, *Pharm. Centralh.*, 1884, No. 59.

² *Analyst*, 2, 98.

cent. of alcohol. If the proportion of alcohol in the ether does not exceed 20 per cent., the ether will be colorless, and the result of the experiment will be correct; but if the proportion of alcohol be above 20 per cent., the layer of ether will be colored and the result below the truth. The absence of color, therefore, indicates the accuracy of the experiment. If the ether is colored, an approximate result can still be obtained by adding 5 cc. of anhydrous ether, and then agitating. It is more satisfactory, however, to dilute a fresh portion of the sample with an equal bulk of pure ether, and use the diluted sample instead of the original. By proceeding in this manner, the proportion of alcohol in mixtures of that liquid with ether can be ascertained within 1 or 2 per cent. with facility. In all cases the proportion of alcohol must be deduced from the reduction in the volume of the ether, and not from the increase in that of the aqueous liquid. Great care must be taken to prevent volatilization of the ether.

Frederking¹ recommended agitation with glycerol instead of water, but the latter is more rapid and generally preferable.

In this connection, it should be mentioned that at 25° C. one volume of ether requires 11.93 volumes of water for solution,² a fact that is not generally recognized in considering the solubility of ether in water. We cannot recommend the method of Allen or the test specified by the Pharmacopoeia of the United States, since, as compared with the elaborated methods previously referred to, they are decidedly deficient in delicacy and accuracy; and if the correct temperature is not maintained, incorrect results will inevitably be obtained.

2. *The Test Based on Extraction with Water and Benzene.*—Fleischer and Frank³ proposed a test which is an elaboration of the preceding one.

They recommended that the specific gravity of the ether may be determined, and that then 10 cc. be shaken in a graduated measure with 5 cc. of benzene and 5 cc. of water. The increase in the volume of the benzene then represents the ether; and the increase in the water volume represents the alcohol plus any water contained in the mixture. The specific gravity of the aqueous alcohol is then determined, and the percentage of alcohol is calculated therefrom.

3. *The Test with "Phosphorized Ether."*—This test, one of no value, the earliest proposed for the detection of alcohol in ether, is based upon an observation by Mrs. Fulhame,⁴ who showed that when ether is boiled on phosphorus, it often deposits crystals on cooling. Agitation with water produces no apparent change in this liquid, but the addition of a little alcohol occasions an immediate turbidity, which gave rise to the statement by Brugnatelli,⁵ that the sophistication of ether by alcohol may be detected

by mixing a few drops of it with "phosphorized ether."

(d) *The Purification of Ether from Alcohol.*—There have been a number of methods proposed for the removal of alcohol from ether. In the case of many of these, the elimination of other impurities is also effected; for example, when an ether containing water and alcohol is treated with sodium, potassium-sodium alloy, phosphoric anhydride, or calcium, not only the water is removed, but, under certain conditions,¹ a part of the alcohol is eliminated as well. Other instances will be referred to when aldehyde is discussed.

Two methods have been suggested for the removal of alcohol alone. The first of these is based on the fact that calcium chloride may be employed for the removal of alcohol as well as water, and consists in extracting the ether with an aqueous solution of the salt;² and the second consists in distilling the ether with about 0.5 per cent. of colophony, which retains the alcohol.³ It is, however, only applicable to an ether containing a small percentage of alcohol and then only when other impurities are absent.

(e) *Other Processes for Making Ethyl Ether.*—In this connection reference should be made to the method devised by Fritsche for the preparation of ether free from alcohol. In this method, gas containing ethylene is treated with sulphuric acid,⁴ and the ethyl sulphuric acid so obtained is converted into ether and sulphuric acid by means of water. This process was operated on a commercial scale in this country for some time, but the industry was destroyed by the Denatured Alcohol Act. Vaporized petroleum was used as a source of ethylene, and natural gas was suggested later, but it was not available in the locality of the plant and it was not considered economical to move the plant. Munroe⁵ proposed erecting a by-product coke plant at the locality, since this furnishes comparatively large amounts of ethylene, but such a step was not taken owing to the inability to secure encouragement from the firm controlling the most suitable by-product coke oven. It is likely, however, that a similar industry may be revived, as natural gas might serve as a suitable material from which to prepare ether.⁷

(f) *Detection of Acetone in Ethyl Ether.*—Acetone occurs largely in some varieties of wood-spirit, and is only a probable impurity in the case of methylic ether. We, therefore, cannot anticipate its presence in ether prepared from pure ethyl alcohol.

Wester⁸ found that the presence of 0.028 per cent. of acetone is readily detected by means of the following test: Three cc. of ether are shaken with a 5 per

¹ Winkler (*Ber.*, **38**, 3612) effected the removal of water from alcohol by means of metallic calcium, but Perkin and Pratt (*Proc. Chem. Soc.*, **23**, 304) have shown that alcohol reacts with calcium. On the Employment of Phosphoric Anhydride, see Perkin, *J. Chem. Soc.*, **45**, 513.

² Fritsch, *Chem.-Ztg.*, **33**, 759. See also Pierre, *Ann. chim. phys.*, [3] **15**, 360, 400.

³ Guigues, *J. Pharm. Chim.*, **24**, 204.

⁴ *Z. anal. Chem.*, **36**, 298; U. S. Patent No. 475,640, Jan. 19, 1897.

⁵ *Bull.*, **92**, U. S. Dept. of Commerce and Labor, Bureau of the Census, **1909**, p. 96.

⁶ Private communication.

⁷ Cf. French Patent 352,687, of 1905, of Lance and Elworthy.

⁸ *Darm. Zentralk.*, **48**, 620.

¹ *Polyt. Notizblatt*, **26**, 48.

² Squibb (*Chem. News*, **51**, 77) found 11.1 volumes of water are required.

³ *Chem.-Ztg.*, **31**, 665.

⁴ "On Combustion," 41.

⁵ *Ann. chim. phys.*, [1] **24**, 73.

cent. aqueous solution of hydroxylamine hydrochloride, then treated, with thorough agitation, with about 4 cc. of sodium hypochlorite solution. In the presence of acetone, the ether layer shows a blue or bluish green tint. Excess of hypochlorite solution should be avoided, but the amount of hydroxylamine hydrochloride solution used is immaterial.

In the *Pharmacopoea Nederlandica*,¹ an interesting test for the detection of acetone is given. Two cc. of the ether are mixed with 6 drops of mercuric chloride solution and 6 cc. of barium hydroxide solution; the clear filtrate is then tested with ammonium sulphide solution, whereby, the presence of the compound $2C_3H_6O \cdot 3HgO$ is made evident.

Other methods for the detection of acetone could be applied in the case of ether, but it is unnecessary to look for such an improbable contaminant at the present time. Acetaldehyde is the only substance other than alcohol which will likely respond to the iodoform test when it is applied to anaesthetic ether.

(To be continued.)

THE ACTION OF ALKALI SALTS UPON PORTLAND CEMENT.

By EDMUND BURKE AND REUBEN M. PINCKNEY.

Received February 10, 1911.

In recent years damage to cement work placed in alkali water has been frequently reported. A usual feature of such damage is that the cement bulges, cracks, and finally crumbles completely. In some cases where the damage has continued to what may be considered its conclusion, the cement has been described as having the appearance and consistency of fresh lime mortar. In every case of which we have reports, the damage can be explained by considering it to be due to internal expansion within the cement mass, which breaks the hold of the cement particles upon one another.

Such damage has been reported from nearly all of the western states, and investigations to discover the cause have been undertaken by the experiment stations of at least three of these states. The investigation here reported occupied about two years' time and was undertaken for the purpose of learning, if possible:

1. Whether the destructive action is really due to "alkali."
2. If so, to which one or what ones of the salts that make up "alkali."
3. To suggest some means whereby the damage may be avoided or lessened.

Examinations² by one of us had shown quite conclusively that in a certain case of damage to a cement sewer, the points of greatest damage coincided with the point where the soil contained the greatest amount of alkali.

In any discussion of the effect of alkali, the first step is obviously to determine what is meant by the term.

ALKALI.

"Alkali," in the popular sense, is a term used to designate the soluble salts that accumulate in regions of little rainfall. Such salts are formed by the decay of rocks and are present in all soils as formed, but with sufficient rainfall and drainage are leached out and removed in the drainage water. They accumulate wherever such alkali-laden waters collect and evaporate, as in the ocean, salt lakes, or soils which receive such drain waters and allow them to evaporate. These accumulations, in the form of more or less concentrated solutions, or as dry salts, may amount to only a few pounds per acre, or in some places become great salt deposits of inches or feet in thickness.

SALTS IN ALKALI.

The salts usually present in greatest amounts in the soils and drain waters of the West are the sulphates, carbonates and chlorides of sodium, magnesium, and, in a smaller amount, of calcium.

The sodium sulphate (which when crystallized with water is sometimes called Glauber's salt) makes up the larger part of the deposits generally known as "white alkali;" usually also there is more or less of the magnesium sulphate (which is also known as Epsom salts).

The so-called "black alkali" is largely sodium carbonate. It is called "black" from its property of dissolving organic matter from the soil, forming dark-colored solutions. This property is not shared by the sulphates, though they are usually present with the sodium carbonate in black alkali. As all these salts are very soluble, they are deposited in solid form only when the drain waters are very much concentrated by evaporation, but they are present in the drain waters of all alkali soils, the white alkali salts being most abundant.

ANALYSES OF ALKALI.

Following are given some analyses of the alkali found in soil at different points where damage to cement work has been reported:

Lab No.	Silica.	Calcium sulphate.	Magnesium sulphate.	Potassium sulphate.	Sodium sulphate.	Sodium nitrate.	Sodium chloride.	Sodium carbonate.
4543	0.110	4.840	23.830	0.540	59.670	0.000	7.860	3.130
304	0.121	2.867	33.398	1.859	59.696	0.000	1.426	0.323
343	1.750	5.470	2.190	2.190	54.700	0.000	12.690	21.000
372	0.550	20.625	17.875	1.237	44.000	2.475	0.000	13.200
392	0.254	12.005	25.387	1.181	56.875	0.000	2.283	1.889
405	0.292	11.546	26.858	1.500	53.799	0.761	04.820	0.401

NOTE.—These analyses, except No. 4543, were made by Dr. F. W. Traphagen and published in Bulletin 18 of the Montana Experiment Station.

In order to determine which of the alkali salts was responsible for the damage to cement work, it was determined to test the effect of the salts separately upon the cement, using first the ones most abundant.

PRELIMINARY TESTS.

A quantity of cement which had been "set" with water and allowed to harden a few weeks was ground

¹ 1905, p. 27.

² See Bulletin 69 of the Montana Experiment Station.

to pass a sieve of one hundred meshes per linear inch. This cement was placed on a filter paper in a Buchner funnel and a saturated solution of sodium sulphate allowed to percolate through it. The filtrate, after passing through the cement, was then examined for any substance that might have been dissolved from the cement. Very small amounts were found, entirely too little to account for the damage, so that no light was thrown upon the problem until it was noted that the filtrate was intensely alkaline. Further tests showed this to be due to sodium hydroxide.

In order to test the matter quantitatively, 50 grams each of a number of different set cements were treated with the sodium sulphate solution, using a 10 per cent. solution to avoid the variation of strength with changes of temperature that had been observed when the saturated solution was employed.

Although a number of different cements were subjected to each treatment reported in this paper, the results were very similar, and hence only a single cement is shown in the analysis. The cement selected for the report is a Portland of good reputation, and is believed to be representative of the best cements upon the market.

Each half liter of the solution filtered through the cement was taken separately and tested by titration for the amount of alkalinity in the filtrate, and the amounts of lime, sulphates, silica, and alumina determined gravimetrically. After two or three liters of the solution had passed through the cement (in about five weeks' time), the cement had a bulged and cracked appearance, similar to that noted in the destruction of cement by natural alkali.

TABLE I.—ANALYSIS OF FILTRATE SECURED BY LEACHING 50 GRAMS SET CEMENT WITH 10 PER CENT. Na_2SO_4 SOLUTION.

	Amount of N/10 acid re- quired to neutralize.	Lime, CaO.	Sulphuric anhydride, SO_3 .
	cc.		
1st 500 cc.....	560	0.3900	24.0300
2nd 500 cc.....	326	0.3800	23.4000
3rd 500 cc.....	262	0.3340	28.4000
4th 500 cc.....	194	0.2480	28.4500
5th 500 cc.....
Total.....	1342	1.3520	104.2800
Present in original solution			112.6831
		1.3520 gain	8.4031 loss

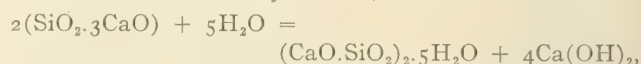
The amount of sodium hydroxide (as shown by the total alkalinity) was high in the first half liter, and rapidly diminished in successive portions, with a corresponding increase of sulphates in the same portions. From this it was evident that a reaction was taking place between the sodium sulphate and some hydroxide present in the set cement. This evidence led us to a consideration of the compounds present in cement, and of the theories that have been propounded in regard to the setting of cement.

Setting of Cement.

COMPOUNDS PRESENT.

So far as we could learn, all investigators agree that in the setting of cement a greater or less amount of calcium hydroxide is formed, which is present in

a crystalline form in the set cement. Le Chatelier states, and others agree, notably the Newberrys and Clifford Richardson, that the important compounds present in cement clinker are tricalcium-silicate ($\text{SiO}_2 \cdot 3\text{CaO}$), and tricalcium-aluminate ($\text{Al}_2\text{O}_3 \cdot 3\text{CaO}$), and Richardson adds "that if only these compounds are present, and in the proportion of six molecules of the silicate to one of the aluminate, the clinker is a pure 'Alit,'" which Tournbohm, a Swedish investigator, has identified as the preponderating mineral constituent of typical cement clinker. Le Chatelier also states, and Richardson agrees, that upon coming in contact with water the tricalcium-silicate reacts to form a lower hydrated silicate and sets free two molecules of calcium hydroxide,



while the tricalcium aluminate reacts with water and a portion of the calcium hydroxide, forming a lower hydrated aluminate,



Richardson states that "The strength of Portland cement after setting is due entirely to crystallized calcium hydrate which binds together the particles of undecomposed cement."

Calculations from these reactions show that if cement had the ideal composition assumed by Richardson the percentages in the unset cement would be: lime (CaO) 71.7 per cent., silica (SiO_2) 22 per cent., alumina (Al_2O_3) 6.2 per cent., which altogether would require for its complete hydration according to the reactions given above 41.7 per cent. of its weight of water; or, in the set cement of that composition, the percentages would be: lime 50.7 per cent., silica 15.6 per cent., alumina 4.4 per cent., water 29.5 per cent. Thus 37.5 per cent. of the weight of the set cement would be calcium hydroxide, $\text{Ca}(\text{OH})_2$.

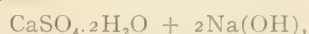
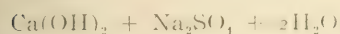
Comparison of the percentages given above with numerous analyses of Portland cement show that commercial cement must contain a large proportion of other constituents of lower lime content than the tricalcium silicate and aluminate, and these lower lime compounds may or may not "hydrate," or take up water when given the opportunity. We do not know how completely the reactions given by Le Chatelier take place, nor the time required before the maximum hydration is accomplished. It seems tolerably well agreed that the reaction involving the aluminate is more rapid at first than that involving the silicate, that is, "The aluminates are responsible for the set, the silicates for the subsequent slower hardening." This would, of course, indicate that the silicate continues to take up water for a considerable period. In fact, practical cement workers have long recognized that it is necessary to keep the cement wet for days or weeks while the hardening is taking place.

Richardson's statement that calcium hydroxide is the binding material of set cement seems to be correct; but, whether so or not, this substance certainly

occupies space in the set cement, and seems to be the only, or, at least, the principal substance in the cement that reacts with the alkali salts (except the sodium carbonate, whose reaction will be discussed later).

GYPSUM FORMED BY ACTION OF SODIUM SULPHATE.

Since the only reaction of which we had any evidence was the interchange between the calcium hydroxide of the cement and the sodium sulphate applied in the solution, forming soluble sodium hydroxide,



we came to the belief that a molecularly equivalent amount of calcium sulphate must be formed, which because of its relative insolubility must remain in the space formerly occupied by the calcium hydroxide. Since we know that calcium sulphate in the presence of water takes the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and that this substance is much used as a cement (plaster of Paris), we were unable to see how the reaction could be so destructive as observation has shown it to be, until we began to consider the relative space that would be occupied by molecular equivalents of calcium hydroxide and gypsum, or even anhydrite, the water-free calcium sulphate.

The molecular weights are: calcium hydroxide Ca(OH)_2 , 74; calcium sulphate (anhydrite) CaSO_4 , 136; gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 172. The specific gravities are: calcium hydroxide, 2.078; calcium sulphate (anhydrite), 2.95 to 2.98; gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 2.32. Then, dividing the molecular weight in grams by the specific gravity, we find the space occupied

by 74 grams of calcium hydroxide to be $\frac{74}{2.078}$, or 35.6 cc. The space occupied by 136 grams (a molecularly equivalent amount) of anhydrite is $\frac{136}{2.98}$ or 45.7 cc. The space occupied by 172

grams of gypsum is $\frac{172}{2.32}$, or 74.1 cc.

These quantities, then, occupy space in the ratios of 35.6 cc., 45.7 cc., and 74.1 cc., or 1.0, 1.28, 2.08. Or, to state the same facts in tabular form:

	Calcium hydroxide, Ca(OH)_2	Anhydrite, CaSO_4	Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
The molecular weights are.....	74.0	136	172.0
The specific gravities are.....	2.078	2.95 to 2.98	2.32
Therefore the space occupied is.....	74	136	172
	2.078	2.98	2.32
Which is.....	35.6	45.7	74.1
Or in the ratio.....	1.0	1.28	2.08

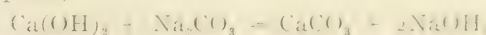
As anhydrite takes up water to form gypsum, the greater ratio, 1 : 2.08, is the final one to be taken into consideration.

This calcium sulphate will certainly act to some extent as a binder; nevertheless, when the calcium hydroxide is replaced by a substance requiring 2.08 times as much space, that substance must exert a disrupting influence, like that observed as the effect of alkali. This expansion, due to an increased amount

of material, is the most important point to be considered in this investigation.

COMPOUNDS RESULTING FROM OTHER REACTIONS.

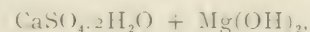
In considering what would be the probable effect of the different salt solutions, we then assumed that if sodium carbonate should be substituted for the sulphate and allowed to act upon the set cement, the resulting compounds would be sodium hydroxide in solution, as in the first case, and calcium carbonate remaining in the space formerly occupied by the calcium hydroxide. This compound will also have some value as a binder, but will likewise exert the same sort of disrupting force, though not in the same degree, as the gypsum. Assuming that the reaction takes place,



the molecular equivalents have the weights:

	Calcium hydroxide, Ca(OH)_2	Calcium carbonate, CaCO_3
The molecular weights are.....	74.0	100
The specific gravities are.....	2.078	2.72
	74	100
The space occupied will be.....	2.078	2.72
Or.....	35.6	36.8
The ratio is.....	1.0	1.03

The action of magnesium sulphate, which occurs in abundance in alkali, will be highly destructive, because both of the compounds resulting from the reaction, magnesium hydroxide,



and gypsum, are but slightly soluble, hence they will both remain in the position formerly occupied by the calcium hydroxide:

	Calcium hydroxide, Ca(OH)_2	Anhydrite + magnesium hydroxide, $\text{CaSO}_4 + \text{Mg(OH)}_2$	Gypsum + magnesium hydroxide, $\text{CaSO}_4 \cdot \text{H}_2\text{O} + \text{Mg(OH)}_2$
The relative molecular weights are.....	74.0	136.0 + 58.0	172.0 + 58.0
The specific gravities are.....	2.078	2.94 + 2.34	2.32 + 2.34
Therefore the relative space occupied is.....	74	136 + $\frac{58}{2.34}$	172 + $\frac{58}{2.34}$
	2.078	2.94	2.32
Which is.....	35.6	71.1	99.0
Or.....	1.0	1.98	2.78

Therefore the relative space occupied will be:

$$\frac{74}{2.078} : \left(\frac{136}{2.94} + \frac{58}{2.34} \right) \quad \left(\frac{172}{2.32} + \frac{58}{2.34} \right)$$

which is 356 : 711 or 356 : 990

1 : 1.98 or 1 : 2.78.

The ratio 1 : 2.78 is the one more probable, as the calcium sulphate tends to take the form of gypsum.

With this ratio before us, it is easy to see why numerous investigators have considered from practical tests that the magnesium salts in sea water are the ones responsible for the damage observed in certain instances.

Some of these investigators have held, that in such cases, new compounds were formed which crystallized, and in the crystallization exerted a pressure that disrupted the cement; that is, they considered

the physical state of the reaction product to be the controlling factor, rather than considering the amount of material present. It seems clear, however, that the amount of material concerned in the reaction can be determined with a fair degree of accuracy, and that the increase in material present sufficiently accounts for the increase in space required, so that the destructive internal strains are explained without resorting to the crystallization theory.

A THEORY OF DISINTEGRATION.

A working theory, then, may be formulated thus: The chemical reaction of alkali that is destructive to cement work is a double decomposition between the various alkali salts and calcium hydroxide, which is an unavoidable constituent, and probably the binding constituent, of all set cement whether the cement is classed as "Portland," "natural," or "slag." This reaction removes a greater or less amount of the calcium hydroxide, the amount depending upon the salts present, the concentration of the solution, the rate of percolation and imperviousness of the cement, and the solubility of the reaction products, and deposits in its place, in most cases, a molecularly equivalent amount of other compounds, which have in some cases cementing properties, but occupy more space than the calcium hydroxide. This *increase of space occupied* disrupts the cement, causing it to bulge, crack, and crumble.

TESTS WITH VARIOUS SALTS.

In order to test this theory we took the cement, set and ground as previously described, placed twenty-five or fifty grams on the Büchner funnel, and added the solution as follows: One-half liter of the solution was placed in a glass-stoppered bottle and poured, a few cc. at a time, upon the cements, and allowed to pass through, using reduced pressure from the filter pump as it becomes necessary, but avoiding it as much as possible in order to avoid loss of water by evaporation from the filtrate. When the half liter had been used the filtrate was returned to the bottle and a fresh supply of the alkali solution provided. Each half liter of the filtrate was thus kept separately and tested separately in order to learn how rapidly the action was proceeding and when it ceased.

A number of different cements were treated in this manner, of which the one selected for complete analysis is believed to be in every way representative.

The samples of cement were obtained directly from the manufacturers, who were informed of the object of the investigation and donated the samples. As they knew the tests would be severe, they undoubtedly provided us with the best cement they were able to manufacture.

THE SALTS USED.

From the first we took care to include samples of the three classes of cements, Portland, slag, and natural. Each cement was treated with the following solutions:

(1) Distilled water, using both 50 grams and 25 grams. Five weeks. This test was made at the same time and on funnels standing beside those with the sodium sulphate.

(2) 10 per cent. sodium sulphate, Na_2SO_4 . This also was tested twice, once using 50 g. of the set cement for each sample, once using 25 grams. Tests continued about five weeks.

(3) 2 per cent. magnesium sulphate, MgSO_4 . Eight weeks. 25-gram samples only.

(4) 2 per cent. sodium carbonate, Na_2CO_3 . Eight weeks. 25-gram samples only.

(5) Sea water. 3.5 per cent. total salts. Eleven weeks. 25-gram samples only.

The funnels were covered with watch glasses to reduce evaporation and to protect the samples from dust, and, except in the case of the first sodium sulphate treatment, the funnels were lightly coated above the sample with vaseline, in order to prevent loss of the salts by creeping over the top. No special attempt was made to protect the cement from contact with the air, and, in fact, in most cases there was an increase in the amount of carbon dioxide present in the sample. There was certainly some loss of water by evaporation, and probably some quantity of soluble salts was retained in the sample, so that the quantitative analyses of the filtrates do not exactly indicate the quantitative changes that have taken place in the solutions. The samples, after treatment with the solutions, were in some cases washed on the funnel with distilled water and the washings analyzed.

The cements, when the salt solutions were added, hardened or "set" in a manner similar to fresh cement when it is treated with water, though the mass did not set so hard after being ground, as fresh cement does. The solution at first percolated rapidly but after a few days the percolation diminished, and in some cases almost entirely ceased, even when the filter pump was used. This slackening occurred before any noticeable bulging or cracking, and in a number of cases, after the disintegration became marked, the rate of percolation again increased.

After the samples had been treated with the salt solutions, they were dried to a more or less nearly air-dry condition, ground and thoroughly mixed, first being freed as completely as might be from the adhering filter paper. An analysis was made of the residue from each treatment. An analysis was also made of the set cement as it was taken for treatment.

The filtrate was analyzed as soon as the half-liter portions had been secured. 25 cc. from each were titrated with N/10 sulphuric acid for total alkalinity; 5, 25, or 50 cc. were taken for gravimetric determination of sulphates (calculated to SO_3); the same for lime (CaO), and usually 100 cc. for silica (SiO_2). In case there was reason to suppose that there was magnesium present in the filtrate, a suitable amount was taken for its determination.

The titration with acid shows approximately the total amount of calcium hydroxide which has reacted

with the salt, forming sodium hydroxide, plus that merely dissolved by the water of the solution. There is a small amount of alkalis dissolved from the cement, as was shown by the examination of the filtrate obtained by leaching the cement with distilled water.

As our alkali salts were all found to contain certain impurities, corrections must be made for the error thus introduced. Our first lot of sodium sulphate contained some magnesium but, as no quantitative estimation was made until this lot had all been used, the amount is not exactly known. Our sodium chloride contained calcium sulphate, therefore our sea water also contained more lime (CaO), more sulphates (SO₃), and more magnesia (MgO) than we intended. When the amount of these impurities is known, the proper correction is made after the totals in the tabulated results of the analyses of the filtrates. The remaining discrepancies are probably due to evaporation and to the error in determination which has been greatly multiplied, in some cases as much as a hundredfold, as, for example, when 5 cc. are taken for the sulphate determination in the 10 per cent. sodium sulphate solution.

Data on the Action of Certain Salt Solutions upon Cement.

TREATMENT OF CEMENTS WITH SODIUM SULPHATE SOLUTION.

Portland cement, 50 grams, was treated as above described. It received four half liters of the 10 per cent. sodium sulphate solution, after which it was dried without washing and prepared for analysis. At the same time a duplicate sample on a funnel beside the first was treated in the same way with distilled water, and the filtrate thus obtained was analyzed in the same way as that from the sodium sulphate treatment.

Following are given the tabulated results of the analyses of the filtrates from both treatments:

TABLE II.—ANALYSIS OF FILTRATE SECURED BY LEACHING 50. G. SET CEMENT WITH DISTILLED WATER, AND WITH 10 PER CENT. SODIUM SULPHATE SOLUTION.

	50 g. cement treated with distilled water.			50 g. cement treated with 10% sodium sulphate solution.		
	N/10 acid required to neutralize. cc.	Calcium oxide (CaO).	Sulphuric anhydride (SO ₃).	N/10 acid required to neutralize. cc.	Calcium oxide (CaO).	Sulphuric anhydride (SO ₃).
1st 500 cc.....	274	0.5200	0.1170	560	0.3900	24.0300
2nd 500 cc.....	214	0.5640	0.0330	326	0.3800	23.4000
3rd 500 cc.....	198	0.5280	0.1030	262	0.3340	28.4000
4th 500 cc.....	176	0.4620	0.0080	194	0.2480	28.4500
Total.....	863	2.0740	0.2610	1342	1.3520	104.2800
Present in original solution.....						112.6831
Loss or gain.....	863 gain	2.0740 gain	0.2610 gain	1342 gain	1.3520 gain	8.4031 loss
From 25 grams.....	432	1.0370	0.1305	671	0.6760	4.2016

Compare this table with Table III.

Upon a study of the analysis of the filtrate obtained by leaching with water, we find that notable amounts of lime (CaO) and of sulphates (SO₃) are present, and that silica is absent from the filtrate. The sulphates and a part of the lime are accounted for by assuming that the gypsum or calcium sulphate (CaSO₄), added by the manufacturer for the purpose of retarding the set, is being dissolved. The rest of the lime is calcium hydroxide dissolved from the set cement, and as the titration with acid is somewhat

more than would indicate that amount of calcium hydroxide, the difference may be accounted for as alkalis dissolved from the cement.

TABLE III.—ANALYSIS OF SET CEMENT, AND OF RESIDUES AFTER LEACHING CEMENT WITH DISTILLED WATER, AND WITH SODIUM SULPHATE SOLUTION.

Treated with	Sodium sulphate.	Distilled water.	Untreated
Moisture.....	0.0755	0.0115	0.0345
CO ₂	0.0490	0.0345	0.0268
Combined water.....	0.0995	0.1370	0.1047
Loss on ignition.....	0.2240	0.1825	0.1660
Silica (SiO ₂).....	0.1655	0.2085	0.1980
Iron oxide (Fe ₂ O ₃).....	0.0800	0.0995	0.0970
Aluminum (Al ₂ O ₃).....			
Lime (CaO).....	0.4000	0.4870	0.4965
Magnesia (MgO).....	0.0118	0.0130	0.0130
Sulphates (SO ₃).....	0.0988	0.0154	0.0155
Potash (K ₂ O).....	0.0017	0.0016	0.0066
Soda (Na ₂ O).....	0.0142	0.0015	0.0045
Total.....	0.9960	1.0090	0.9971

Since no silica was added to the cement in the solutions, and none appears in the filtrate, the total amount of silica must remain as it was before the treatment, which amount is shown by the analyses of the untreated cement. Since this total amount remains unchanged, the weight of the cement residue after treatment may be found by dividing the amount of silica by the percentage of silica found in the residue. As would be expected, there is a loss in weight (of residue) when cements are leached with water, as is shown in Table IV, etc.

In order to check the accuracy of the analysis of the filtrate, the total solids were determined in 50 cc. portions of the several filtrates, first treating with excess of carbon dioxide in order to convert the hydroxides into carbonates. (Since the solution had been exposed to the air it had probably already taken up some carbon dioxide, hence would weigh too heavy to be calculated as hydroxides.) The total solids as

TABLE IV.—AMOUNT OF MATERIAL IN RESIDUE OBTAINED BY TREATING SET CEMENT WITH DISTILLED WATER.

	Grams.
Silica in cement before treatment (19.80 per cent).....	4.9500
Weight of cement after treatment (silica = 20.85 per cent.).....	23.7410
Weight of cement before treatment.....	25.0000
Loss in weight.....	1.2590
Dry weight before treatment (water = 3.45 per cent).....	24.1375
Dry weight after treatment (water = 1.15 per cent).....	23.4680
Loss in dry matter.....	0.6695

	Grams.
Ignited weight before treatment (loss = 16.60 per cent.)	20.8500
Ignited weight after treatment (loss = 18.25 per cent.)	19.4083
Loss in ignited matter	1.4417

	Before.	After.	Loss.
Calcium oxide (CaO)	12.4125	11.5629	0.8496
Sulphuric anhydride (SO ₃)	0.3875	0.3656	0.0219
Potassium oxide (K ₂ O)	0.2775	0.0736	0.2039
Sodium oxide (Na ₂ O)			
Loss		1.0754	1.0754
Error			0.3663

calculated from the analysis should be as follows:
Calculated from analysis, in 50 cc., filtrate from leaching with water, 4th half-liter:

	Gram.
0.0462 gram CaO	Indicates 0.0825
Alkalinity 1.1 cc. N/10	" 0.0055
0.0008 SO ₃	" 0.0015
	0.0895
Found by direct weighing	0.0926
Error	0.0031

In 50 cc. filtrate from leaching with sodium sulphate solution, 4th half-liter:

	Grams.
0.0248 gram CaO	Indicates 0.0443
NaOH equivalent to 12.4 cc. N/10	" 0.0657
2.8450 gram SO ₃	" 5.0499
	5.1599
Found by direct weighing	5.1076
Error	0.0523

The analysis of the residue left after leaching with water confirms that of the filtrates by showing that the change consists in a loss of lime (CaO), sulphates (SO₃), and alkalis (K₂O and Na₂O). The treatment with water in no case caused any cracking or bulging, but may have weakened the cement by removal of the binding material, calcium hydroxide, unless the additional amount set free by the further hydration of the cement was sufficient to offset this loss.

The analysis of the filtrate, left after leaching with sodium sulphate, shows a considerable amount of lime (CaO), a smaller amount of sulphate (SO₃) than was present in the solution as it was applied to the cement, and a great amount of sodium hydroxide.

This sodium hydroxide can be formed only by the interaction of the sodium sulphate with some hydroxide present in the cement. The only hydroxide present in set cement in any quantity is the calcium hydroxide, which Richardson has shown to be the binding material. Therefore the calcium hydroxide must be acted upon by the sodium sulphate. On the other hand, the loss of the sulphate ions from the solution shows that some insoluble sulphate is being formed and retained in the residue. The only one of the metallic elements present in the cement (calcium, aluminium, iron, etc.) that forms an insoluble sulphate is the calcium, hence calcium sulphate must be the reaction product.

The corresponding residue shows a loss of lime (CaO), a gain in sulphates (SO₃), a very slight gain

in magnesia (MgO), and a gain in alkalis (K₂O and Na₂O); the alkalis we feel sure would not show this gain if the residues had been well washed with water after the treatment with the sodium sulphate solution.

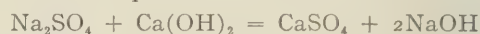
Taking into consideration the fact that changes due to evaporation and to "creeping" rendered discrepancies in the analysis of the filtrates inevitable, it is believed that the analysis of the residue is more nearly accurate than that of the filtrate.

In order to learn the effect of sodium sulphate upon the amount of material present, compare Tables IV and V.

TABLE V—AMOUNT OF MATERIAL IN RESIDUE OBTAINED BY LEACHING SET CEMENT WITH SODIUM SULPHATE SOLUTION.

	Grams.
Silica in original cement (19.80 per cent.)	4.9500
Weight of cement after treatment (silica = 16.56 per cent.)	29.8914
Weight of cement before treatment	25.0000
Increase in weight	4.8914
Dry weight before treatment (water = 3.45 per cent.)	24.1375
Dry weight after treatment (water = 7.50 per cent.)	27.6495
Increase in dry matter	3.5120
Ignited weight before treatment (loss = 16.60 per cent.)	20.8500
Ignited weight after treatment (loss = 22.40 per cent.)	23.1957
Increase in ignited matter	2.3457
	Before. After. Loss. Gain.
Sulphuric anhydride (SO ₃)	0.3875 2.9534 2.5659
Calcium oxide (CaO)	12.4125 11.9566 0.4559
Potassium oxide (K ₂ O)	0.2275 0.4753 0.1978
Sodium oxide (Na ₂ O)	
	0.4559 2.7637
	-0.4559
Net gain	2.3078
Error	0.0379

The analyses of filtrate and residue point to the same conclusion, namely, that the chemical reaction of the sodium sulphate is



with the calcium hydroxide, and that the greater part of the calcium sulphate remains in the residue. The bulging and cracking were well marked, resembling those observed in cement work attacked by alkali.

EFFECT OF THE REACTION UPON SPACE OCCUPIED BY THE CEMENT.

It is interesting at this point to consider the relative space occupied by the reaction product which has accumulated in the cement residue (as shown by the analyses), compared with that occupied by the calcium hydroxide before the treatment. To make this comparison, we must consider not only the lime transformed from hydroxide into gypsum, but also that removed from the cement in the filtrate, leaving its space to be filled before the reaction product can exert any disrupting force.

Since calcium hydroxide, Ca(OH)₂, has the specific gravity 2.078, 1 gram calcium hydroxide occupies 1/2.078 or 0.496 cc. space. 1 gram sulphur trioxide (SO₃) combines with 74/80 gram Ca(OH)₂, and water to form gypsum, with an increase in volume over

that required by the lime in the ratio 1 : 2.08, as previously pointed out; then for every gram of SO_3 accumulated, there must be an increase of $74/80 \times 1.08/1 \times 0.496 = 0.48$ cc. in space occupied, and since 1 gram lime (CaO) in the form of hydroxide $\text{Ca}(\text{OH})_2$ requires $74/56 \times 0.496$ cc., or 0.656 cc. space, for every gram of lime removed from the cement there must be a loss of 0.656 cc. in space occupied. The amounts of the various constituents respectively removed from, and accumulated in, the residues are computed in Table V.

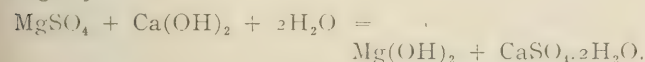
From these amounts we find that 25 grams of cement lost 0.46 gram lime (CaO) and accumulated 2.57 grams sulphate (SO_3).

∴ Space increase in the cement equals $(2.57 \times 0.48 \text{ cc.}) - (0.46 \times 0.656 \text{ cc.})$, or 0.93 cc.

We now turn to the next treatment, which was with magnesium sulphate.

TREATMENT WITH MAGNESIUM SULPHATE SOLUTION.

The 25-gram sample was treated with 2 per cent. solution, the treatment taking about eight weeks' time. The analysis of the filtrate obtained showed that the filtrate was only slightly alkaline, as but 64 cc. of N/10 acid were required to neutralize the whole of the filtrate. This does not indicate that the calcium hydroxide is not attacked, but only that the reaction products are retained in the residue, as both gypsum and magnesium hydroxide are relatively insoluble in alkaline solutions, and our solution is slightly alkaline.



Hence we should expect to find what in fact we do find, that considerable amounts of magnesia (MgO) and of sulphate (SO_3) are lost from the solution, and the analysis of the residue shows that they are accumulated in the residue.

TABLE VI.—ANALYSIS OF FILTRATE SECURED BY LEACHING 25 GRAMS CEMENT WITH 2 PER CENT. MAGNESIUM SULPHATE SOLUTION.

	N/10 acid re- quired to neu- tralize. cc.	Calcium oxide, (CaO). Gram.	Sulphuric anhydride (SO_3). Grams.	Magnesia (MgO). Grams.
1st 500 cc.....	6	0.2780	5.6260	2.6060
2nd 500 cc.....	10	0.2680	6.4900	3.0680
3rd 500 cc.....	10	0.2400	7.0260	3.4420
4th 500 cc.....	8	0.2520	7.2740	3.4400
5th 500 cc.....	10	0.2100	7.4940	3.6020
6th 500 cc.....	10	0.1780	7.3860	3.5460
Total.....	54	1.4260	41.2960	19.7040
Washings.....	10	0.0800	0.2740	0.0700
Total.....	64	1.5060	41.5700	19.7740
Present in original solution...	—	—	45.0000	22.1400
Difference.....	—	1.5060	3.4300	2.3660

The amounts of magnesia and sulphates are not molecularly equivalent, but if, after deducting from the lime removed an amount sufficient to account for the total alkalinity of the filtrate, we consider the rest of that lime as combined with SO_3 to form calcium sulphate, the amount of sulphate so accounted for, added to that retained in the residue, is nearly

the molecular equivalent of the magnesia retained. This indicates that the reaction given is the correct one and takes place freely. The magnesium hydroxide $\text{Mg}(\text{OH})_2$ formed is almost completely insoluble, therefore most of it remains with the residue. The calcium sulphate formed is somewhat more soluble and a portion is carried off in the filtrate, though a considerable portion of this compound also is retained in the residue.

TABLE VII.—ANALYSIS OF RESIDUE OBTAINED BY LEACHING CEMENT WITH 2 PER CENT. MAGNESIUM SULPHATE SOLUTION.

Treated with	Magnesium sulphate.
Moisture.....	0.1480
Carbon dioxide (CO_2).....	0.0185
Combined water.....	0.1135
Loss on ignition.....	0.2700
Silica (SiO_2).....	6.1425
Alumina and iron oxide (Al_2O_3 , Fe_2O_3).....	0.0725
Lime (CaO).....	0.3270
Magnesia (MgO).....	0.0836
Sulphates (SO_3).....	0.1139
Potash (K_2O).....	0.0015
Soda (Na_2O).....	0.0027
Total.....	1.0137

TABLE VIII.—AMOUNT OF MATERIAL IN RESIDUE OBTAINED BY LEACHING 25 GRAMS CEMENT WITH 2 PER CENT. MAGNESIUM SULPHATE SOLUTION.

	Grams.
Total weight of silica in cement (19.80 per cent.).....	4.9500
Original weight of cement.....	25.0000
Weight of cement after treatment (silica = 14.25 per cent.)....	34.7361
Increase in weight.....	9.7361
Dry weight before treatment (water = 3.45 per cent.).....	24.1375
Dry weight after treatment (water = 13.80 per cent.).....	29.9425
Increase in dry weight.....	5.8050
Ignited weight before treatment (loss = 16.60 per cent.).....	20.8500
Ignited weight after treatment (loss = 27.80 per cent.).....	25.3574
Increase in ignited matter.....	4.5074

	Before.	After.	Loss.	Gain.
Sulphuric anhydride (SO_3).....	0.3875	3.9564	3.5689
Magnesium oxide (MgO).....	0.3250	2.9039	2.5789
Calcium oxide (CaO).....	12.4125	11.3581	1.0538
Potassium oxide (K_2O) } Sodium oxide (Na_2O) }	0.2775	0.1459	0.1316
			1.1854	6.1478
			1.1854	1.1854
Net gain.....			4.9624	4.9624
Error.....			0.4550

Below is given an attempt to balance the magnesia and sulphuric anhydride concerned in the reaction:

In Table VIII we find a gain in magnesia (MgO).....	2.5789
in sulphuric anhydride (SO_3).....	3.5689
a loss in lime (CaO).....	1.0544

Total alkalinity of filtrate and washings = 64 cc. N/10 acid, which would amount to 0.1792 gram lime.

Deducting this amount from the amount of lime lost from the residue, we have 0.8752 gram lime present in the filtrate as calcium sulphate (CaSO_4), indicating 1.2503 grams SO_3 . This, added to that noted in the residue, makes 4.8192 grams SO_3 , which indicates 2.4096 grams magnesia, a discrepancy of 0.1693

gram. This discrepancy is only partially accounted for by taking into account the slight solubility of the magnesium hydroxide. The amount which might be dissolved and remain in the filtrate as magnesium hydroxide would be small, and is variously reported by different observers (see Comey, *Dictionary of Chemical Solubilities*, pp. 216, 217), from one part in 5142 parts water, to one in 100,000. It is also reported that calcium hydroxide and calcium sulphate, which are present in our filtrate, do not diminish the solubility, while sodium chloride and sodium sulphate, and potassium chloride and potassium sulphate, some of which are present by being dissolved from the alkalis of the cement, increase the solubility. The highest solubility quoted by Comey would allow 0.5835 gram magnesia (MgO) to be contained as the hydroxide, $Mg(OH)_2$, in the three liters of filtrate, but it would seem that if so much were present, it would be shown by the titration. In this treatment also we have no evidence of other reactions than that of the salt solution upon the calcium hydroxide.

TREATMENT WITH SODIUM CARBONATE SOLUTION.

The treatment with this solution was continued for about eight weeks, using a 2 per cent. solution of sodium carbonate (Na_2CO_3). The results of the analysis of the filtrate were about as we had expected from the behavior of the sodium sulphate and magnesium sulphate, except that considerable amounts of silica (SiO_2) were found in the filtrate, together with a smaller amount of alumina. As was expected, no lime was found in the filtrate, the calcium carbonate formed from the calcium hydroxide being almost completely insoluble. Since the sodium carbonate, which is alkaline to titration, is in this reaction replaced by an equivalent amount of sodium hydroxide,



there should be no change detected by titration for alkalinity before and after the solution has percolated through the cement. In fact there was a slight increase shown, probably caused by evaporation of the filtrate. Large amounts of carbon dioxide were removed from the filtrate, which seems to indicate

the usual exchange, while the silica and alumina in the filtrate indicates that the silicates and aluminates are being attacked, forming soluble sodium or sodium aluminum silicates, as well as the insoluble calcium carbonate and the soluble sodium hydroxide.

A comparison of the analysis of the filtrate with that of the residue shows that while a considerable amount of carbon dioxide is removed from the solutions, a greater amount is accumulated in the residues, indicating that a portion of the carbon dioxide (CO_2) has been taken up from the air.

TABLE X.—ANALYSIS OF RESIDUE LEFT AFTER LEACHING 25 GRAMS CEMENT WITH SODIUM CARBONATE.

Treated with	Sodium carbonate.
Moisture.....	0.0845
Carbon dioxide (CO_2).....	0.1678
Combined water.....	0.0677
Loss on ignition.....	0.3200
Silica (SiO_2).....	0.1350
Alumina and iron oxide (Al_2O_3 , Fe_2O_3).....	0.0960
Lime (CaO).....	0.4285
Magnesia (MgO).....	0.0042
Sulphates (SO_3).....	0.0036
Potash (K_2O).....	0.0019
Soda (Na_2O).....	0.0063
Total.....	0.9955

TABLE XI.—AMOUNT OF MATERIAL IN RESIDUE OBTAINED BY LEACHING 25 GRAMS CEMENT WITH 2 PER CENT. SODIUM CARBONATE SOLUTION.

	Grams.	Grams.
Weight of cement before treatment.....		25.0000
Lime in cement before treatment.....	12.5000	
Lime removed in filtrate.....	0.0130	
Lime remaining in residue.....	12.4870	
Weight of cement after treatment (lime = 42.75 per cent.).....		29.2091
Increase in weight.....		4.2091
Dry weight before treatment (water = 3.45 per cent.).....		24.1375
Dry weight after treatment (water = 8.50 per cent.).....		26.7263
Increase in dry matter.....		1.5888
Weight of ignited matter before treatment (loss = 16.80 per cent.).....		20.8500
Weight of ignited matter after treatment (loss = 32.30 per cent.).....		19.8038
Loss in ignited matter.....		1.0462
Silica (SiO_2) removed in solution.....	1.0830	
Calcium oxide (CaO) removed in solution.....	0.0130	
Aluminum oxide (Al_2O_3) removed in solution.....	0.0315	
Magnesium oxide (MgO) removed in solution.....	0.0170	
Sulphuric anhydride (SO_3) removed in solution.....	0.0080	
	1.1525	1.1525
Error.....		0.1063

TABLE IX.—ANALYSIS OF FILTRATE SECURED BY LEACHING 25 GRAMS CEMENT WITH 2 PER CENT. SODIUM CARBONATE SOLUTION.

	N/10 Acid required to neutralize. cc.	Carbon dioxide (CO_2).
1st 500 cc.....	1234	1.6000
2nd 500 cc.....	1250	2.7400
3rd 500 cc.....	1278	2.5100
4th 500 cc.....	1252	2.4700
5th 500 cc.....	1254	2.4000
6th 500 cc.....	1264	2.3400
7th 500 cc.....	1234	2.3540
Washings.....	68	0.1800
Total.....	8834	16.5940
Present in original solution.....	8520	18.6480
Difference.....	314	-2.0540
Composite.....	$\left\{ \begin{array}{l} Al_2O_3 \\ SiO_2 \\ SO_3 \\ MgO \end{array} \right.$	$\left\{ \begin{array}{l} 0.315 \\ 1.0830 \\ 0.1800 \\ 0.0300 \end{array} \right.$

It is not possible to say with certainty whether this carbon dioxide is withdrawn from the air by the union of the carbon dioxide, CO_2 , with calcium hydroxide, $Ca(OH)_2$, in the residue, or with the soluble sodium hydroxide ($NaOH$) which is ultimately found for the most part in the filtrate, but it is probable that both reactions take place to some extent, in proportions depending upon factors of concentration and circulation of the air containing carbon dioxide. Of course the sodium carbonate formed by this reaction, if it afterwards comes in contact,



with the calcium hydroxide ($\text{Ca}(\text{OH})_2$), will react as freely as that originally applied in the solution. As no other solution besides the sodium carbonate invariably removed silica from the cement, and all the solutions may contain sodium carbonate, if, after reacting with the calcium hydroxide, forming sodium hydroxide, the solution comes in contact with air containing carbon dioxide, it seems likely that the small amount of silica which was sometimes found in filtrates from any of the treatments (except that with magnesium sulphate) was entirely due to the action upon the cement of sodium carbonate, and not to that of the salt solution that was being intentionally applied. As all the samples were exposed to the air while upon the funnels, and all show a considerable increase in CO_2 , there would certainly be opportunity for the sodium carbonate to be formed. The interaction of calcium hydroxide and sodium carbonate, as above pointed out, causes little increase in space occupied, and, taking into account the material removed (silica and alumina), it is probably true that there is *no* increase in space occupied.

TREATMENT WITH SEA WATER.

The sea water used in the treatment next discussed was made by dissolving these amounts of various dry salts:

COMPOSITION OF THE ARTIFICIAL SEA WATER.

Potassium bromide (KBr).....	3.96	Grams
Sodium chloride (NaCl).....	1100.00	"
Potassium sulphate (K_2SO_4).....	35.00	"
Calcium sulphate (CaSO_4).....	57.12	"
Magnesium sulphate (MgSO_4).....	57.84	"
Magnesium chloride (MgCl_2).....	151.85	"
Magnesium carbonate (MgCO_3).....	4.22	"
Distilled water.....	40.0	Liters

These amounts were calculated from the analyses quoted by Thorp (*Dictionary of Applied Chemistry*, Vol. III, p. 960). A partial analysis of this sea water showed that 100 cc. contained:

	Gram.
Lime (CaO).....	0.0738
Sulphate (SO_3).....	0.2548
Magnesia (MgO).....	0.2001

The cement was treated in the Buchner funnel for about six weeks in the manner previously described, then the work was interrupted for one month, and resumed with a further treatment of five weeks, so that the cement remained on the funnel for about fifteen weeks and was treated for about eleven weeks, considerably longer than was the case with other solutions.

The portions of the filtrate were analyzed for total alkalinity, sulphates (SO_3), lime (CaO), magnesia (MgO), and silica (SiO_2). Silica was found in some portions and absent from others, although all the sea water was taken from the same carboy. The filtrate was only slightly alkaline, but had gained considerable amounts of lime, and lost sulphates and magnesia as in the case of the magnesium sulphate treatment noted above.

TABLE XII.—ANALYSIS OF FILTRATE SECURED BY LEACHING 25 GRAMS CEMENT WITH SEA WATER.

	Total alkalinity.	Calcium oxide (CaO).	Sulphuric anhydride (SO_3).	Magnesium oxide (MgO).
1st 500 cc.....	134	1.3880	0.5320	0.0100
2nd 500 cc.....	4	1.4480	1.1946	0.3520
3rd 500 cc.....	none	0.8420	1.2900	0.7020
4th 500 cc.....	2	0.7560	1.2140	0.7600
5th 500 cc.....	1	0.8700	1.2000	0.5780
6th 500 cc.....	1	0.3580	1.2500	0.9740
7th 500 cc.....	none	0.3580	1.2800	0.8660
8th 500 cc.....	none	0.4080	1.3240	0.9160
Total.....	142	6.4280	9.2840	5.1580
Present in orig. soln....		2.9500	10.1920	8.0000
		3.4780 gain	0.9080 loss	2.8420 loss

TABLE XIII.—ANALYSIS OF RESIDUE SECURED BY LEACHING 25 GRAMS SET CEMENT WITH SEA WATER.

Treated with	Sea water.
Moisture.....	0.0820
Carbon dioxide (CO_2).....	0.0705
Combined water.....	0.1335
Loss on ignition.....	0.2860
Silica (SiO_2).....	0.1648
Iron and alumina (Fe_2O_3 , Al_2O_3).....	0.0890
Lime (CaO).....	0.3200
Magnesia (MgO).....	0.0900
Sulphates (SO_3).....	0.0430
Poash (K_2O).....	0.0017
Soda (Na_2O).....	0.0061
Total.....	1.0006

TABLE XIV.—AMOUNT OF MATERIAL IN RESIDUE SECURED BY LEACHING 25 GRAMS CEMENT WITH SEA WATER.

	Grams.
Silica in cement before treatment (19.80 per cent.).....	4.9500
Weight of cement after treatment (silica = 16.49 per cent.)....	30.0182
Original weight of cement.....	25.0000
Increase in weight.....	5.0182
Dry weight before treatment.....	24.1375
Dry weight after treatment (water = 8.25 per cent.).....	24.5417
Increase in dry weight.....	3.4042
Ignited weight before treatment (loss = 16.60 per cent.).....	20.8500
Ignited weight after treatment (loss = 28.60 per cent.).....	21.4330
Increase in ignited weight.....	0.5830
	Before. After. Loss. Gain.
Calcium oxide (CaO).....	12.4175 9.6058 2.8117
Sulphuric anhydride (SO ₃).....	0.3875 1.2908 0.9033
Magnesium oxide (MgO)...	0.3250 2.7016 2.3766
Potassium oxide (K ₂ O) } ...	0.2775 0.2341 0.0434
Sodium oxide (Na ₂ O) }	
	2.8551 3.2799
	2.8551
Net gain.....	0.4248 0.4248
Error.....	0.1682

The residue, on the other hand, has increased in magnesia and in sulphates, and has lost lime. The ratios among these substances are such as to indicate that not all the change is due to interaction between the calcium hydroxide and magnesium sulphate, but some of the magnesium chloride in the sea water must have taken part in the reaction as well.

In this treatment with sea water, we have a solution that is essentially similar to the natural alkali

RECAPITULATION.

LABORATORY OF THE AGRICULTURAL
EXPERIMENT STATION,
BOZEMAN, MONTANA.

By WM. M. BOOTH, Chemical Engineer, Syracuse, N. Y.

BOILER WATERS.

TABLE I.—BOILER WATER PURIFICATION.

Synopsis

1. *General*—Relating to the quality of water.
2. *Scaling*—Corrosion, priming, foaming.
3. *Mechanical Filtration*.
 1. Clear water basin; bars.
 2. Screens.
 3. Settling tanks in duplicate.
 4. Filters {
 - Sand.
 - Coke.
 - Wood.
 - Hot well.
 - Open heater.
 - Closed heater, pressure. {
 - a tubes.
 - b drips.
4. *Thermal*.

External	Live steam heater.
	External sand filters.
	Economizers.
	Fire box heater.
	Mud drum.
Internal	Internal heater.
	Skimmer, dome-funnel.
5. *Thermo-Physical*.

Internal boiler purgers, coal dust, sawdust, kerosene, starch.
6. *Thermo-Chemical, soda*.
 - (a) Harrison.
 - (b) Bonnell.

Electro-Chemical, zinc-balls, aluminum.
8. *Chemical*—Internal, boiler compounds.
9. *Chemical*—External.
 - (a) Intermittent.
 - (b) Continuous.
 - (c) Intermittent and continuous.
10. *Specific Instances*.

TABLE II. -BOILER WATERS CLASSIFIED ACCORDING TO QUANTITY OF SCALE-FORMING SOLIDS.

Soft—To 50 parts per million.

- (a) Rain or snow.
- (b) Water from granite or quartz rock regions.
- (c) Returned water.
- (d) Swamps.
- (e) Lakes.
- (f) Large rivers.

Hard—Above 85 parts per million.

- (a) Springs.
- (b) Lakes.
- (c) Small rivers and creeks.
- (d) Wells.

Saline—Containing above 170 parts per million chlorides, of Ca, Mg, Na or K.

- (a) Sea.
- (b) Wells.
- (c) Mineral springs.

Alkaline—Carbonates or bicarbonates of the alkalies.

- (a) Western plains.
(b) Springs.

Acid—Containing any strong mineral acid.

TABLE III.—BOILER WATER TREATMENT.

To 50 Parts per Million—Thermal.

From 50--170 Parts per Million:

1. Heaters.
2. Lime.
3. Soda, hot or cold.
4. Caustic soda.
5. Phosphate of soda.

From 170-250 Parts per Million:

1. Soda and heat.
2. Lime and soda ash.
3. Caustic soda and soda ash.

From 250-340 Parts per Million:

1. Soda and heat.
2. Lime and soda.

From 340-680 Parts per Million:

1. Heat and soda.
2. Lime and soda.

From 680-1020 Parts per Million:

1. Lime and soda.
2. Barium compounds.

From 1020-5100 Parts per Million:

1. Lime and soda.
2. Barium compounds.

Few eastern waters are alkaline to phenolphthalein before boiling (fourth group Table II). Those west of the Mississippi river often contain carbonates and bicarbonates of the alkalis with sulphate and chloride of soda. The treatment of such waters is very difficult.

Natural waters seldom have an acid reaction (fifth group Table II) due to the presence of a strong mineral acid. The water from coal mines may, however, carry sulphuric acid, and waters from springs are sometimes charged with hydrogen sulphide.

All waters contain carbon dioxide, sometimes in considerable quantity, and I believe that this is the basis of many boiler troubles.

Any natural water may contain organic matter, gases, suspended solids and dissolved minerals. We are not able to discuss the boiler reactions of any of these but the latter. Much study must be put on the others. Nor are we very sure of the action of dissolved minerals under the intricate processes of steam production. Their removal is an accomplished fact. The apparatus devised for such removal will now occupy our attention.

BOILER WATERS.

Steam waters are seldom free from suspended solids those from deep wells being the exception. Running streams carry sand, clay decomposing vegetable matter sewage and trade wastes. This is particularly true of rivers upon the banks of which our larger industries are found. Waters of this character, subject to rapid changes, should generally be led into settling basins (Fig. 1) or at least strained before passing to the pump. The simplest method of treatment is a wing dam (Fig. 2) placed nearly across the forebay in such a way that the intake water is drawn from a quiet pool at medium depth. Floating matter including grease and water plants is eliminated. Even with such precautions a screen is required (Fig. 3). This may be of copper or bronze and is furnished in many shapes—conical, cylindrical, or plain, set in a series of frames. These screens should remove the grosser suspended matter. The finer the mesh the better, consistent with working conditions provided the plant is running condensing.

If the water contains oil, a sand, coke or wood-fiber filter (Fig. 4) will be advantageous. I have found a 36-inch sand filter very useful in the removal of the sludge of wool-washing machines.

Considerable sewage and organic matter can be taken out with coke which should be broken to a coarse powder. Some engineers think coke softens water, chemists know differently.

Assuming that the water has passed the pumps reasonably clean which should always be the case, we usually find the closed heater (Fig. 5) next in line.

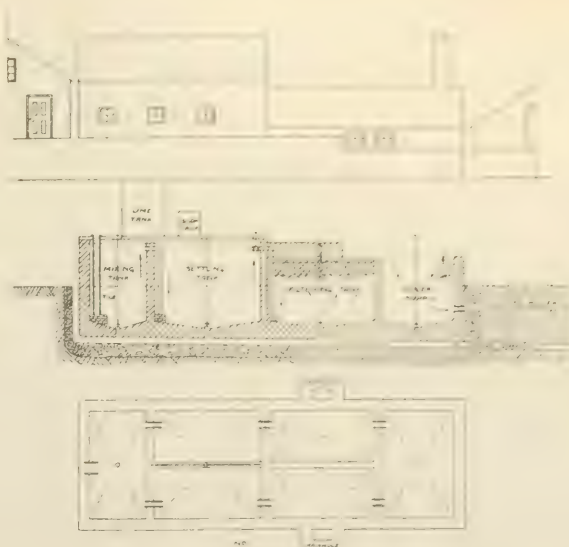


Fig. 1.

With steam on one side and raw cold water on the other the bicarbonates of calcium and magnesium are partially decomposed. Depending upon the speed with which the water is driven through the heater tubes, and the amount of heat supplied by the condensing steam the separated monocarbonates either lodge where they are set free or are driven into the

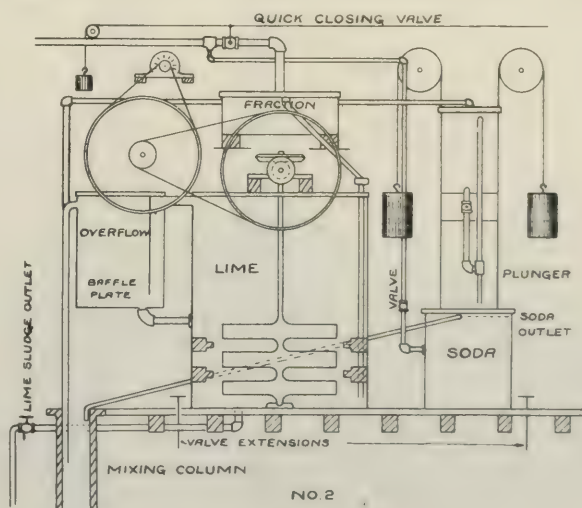


Fig. 2.

boiler, the reaction being continuous from the moment heat is applied. I often find the tubes of such apparatus and the boiler supply pipe filled with scale to a point where the water will scarcely pass. Such suspended matter as enters the boiler circulates with the water for a time and finally deposits or is blown out as sludge.

FIG. 1

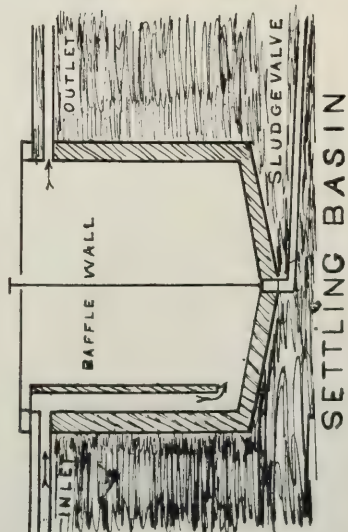


FIG. 4

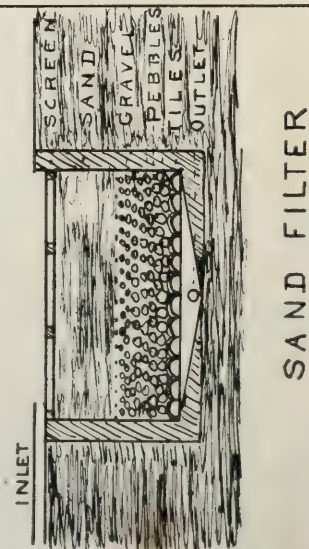


FIG. 2

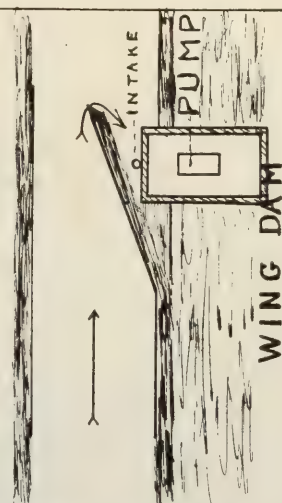


FIG. 3

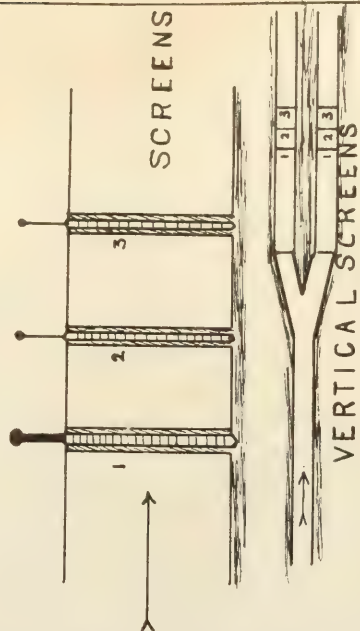


FIG. 5

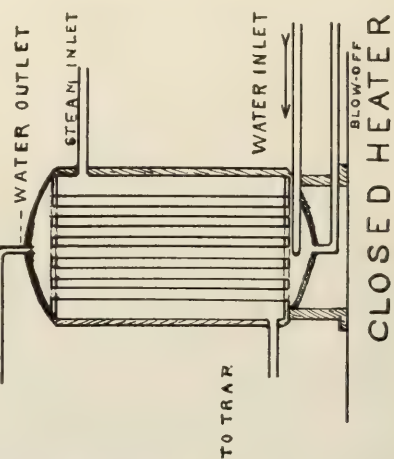


FIG. 6

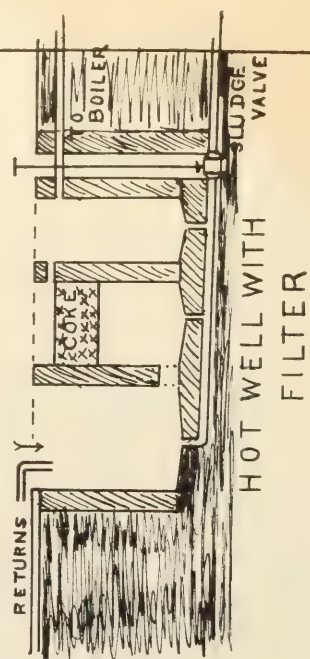
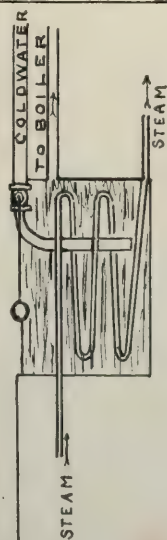
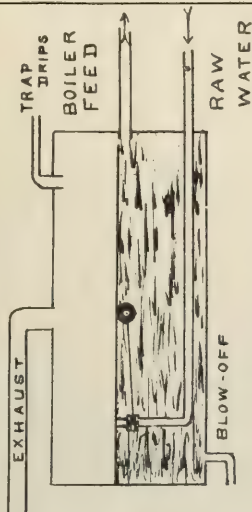


FIG. 7



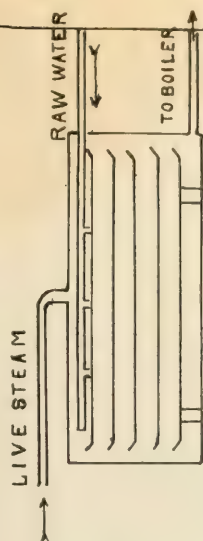
SIMPLE
OPEN HEATER

FIG. 8



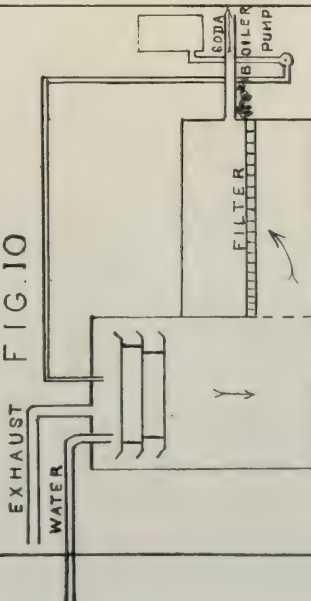
CLOSED
HOT WELL

FIG. 9



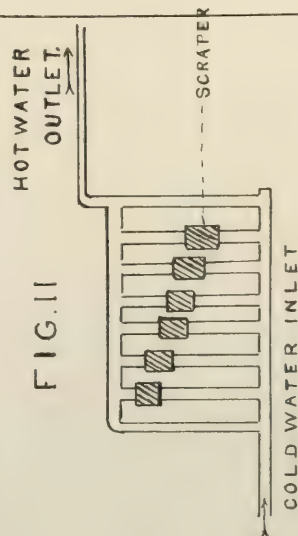
LIVE STEAM HEATER
AND
PURIFIER

FIG. 10



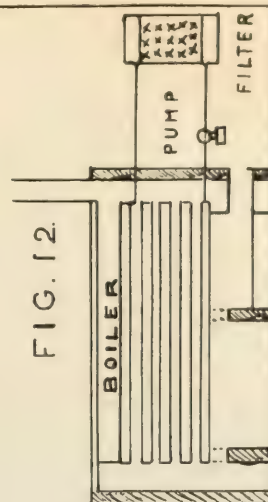
HEATER AND
PURIFIER

FIG. 11



ECONOMIZER

FIG. 12



DE-SCALING
DEVICE

The closed heater is a thermal purifier of uncertain action and its efficiency may approach zero when the tubes are scaled on one side and fouled with oil on the other.

I sometimes find hot wells (Fig. 6), some at atmospheric, others under steam pressure. In either instance raw water exhaust steam and return drips from the pumps and heating system are mixed. The thermal purification is begun at this point by a partial decomposition of carbonates.

In one instance the exhaust steam from several engines passes through two-inch tubes around which the raw boiler water flows on its way to the pump (see figure). These tubes collect scale rapidly in the hard water used.

The *live* steam purifiers (Fig. 9) take advantage of the insolubility of carbonates and gypsum at boiler pressures. Generally cylindrical in form this apparatus admits steam below or at the side of and water above removable trays. The scale separates from the thin layer of heated liquid. Periodically the trays are removed and cleaned.

In order that a live steam heater may be sufficient the temperature must be high, the circulation excellent and not too rapid. We have found 50 per cent. of the sulphates and 75 per cent. of the carbonates of hard water removed by this method.

An ingenious purifying apparatus (Fig. 12) consists of a sand filter connected with the boiler under pressure and through which the water is constantly pumped. Suspended matter is filtered out.

The economizer (Fig. 11) is one of our best efficient descalers as the temperature is often as high as 300° F. Such apparatus is really an auxiliary boiler.

Various devices have been gotten up to purify water by passing it through or at the side of the fire-box or bridge wall before entering the boiler. The difficulty with all classes of closed heating and descaling devices is their lack of cleaning facilities. Such heaters need as much scraping inside as the tubes of economizers.

The mud drum of the water tube boiler answers a double purpose—the collection and removal of precipitated calcium and magnesium compounds and of mud. If for no other reason, the water tube type boiler has large advantage over others due to this construction.

Still another type of thermal purifiers is placed in the boiler itself. One of the simplest of these is a cylinder about 10 inches in diameter running the length of, and immediately above, the flues. Raw water is admitted at one end and traverses the heated tube under boiler pressure and is delivered at the opposite end where it spreads out at the upper water level. This is useful in very hard water sections. This tube is cleaned by a steam jet daily.

Finally internal water purification is assisted by revolving or rocking buckets that scoop up the separated sludge.

Many practical men use coal dust, sawdust or starch-bearing vegetables in boilers. Potatoes have been used extensively. In any such instance an attempt is

made to furnish artificial centers of attraction for the depositing scale or to include colloidal materials that will prevent the formation of dense deposits. Logwood, chestnut and oak sawdust have answered the purpose sought.

Regarding the action of kerosene we have no theory. It is used in large plants very successfully. The liquid is added to the water, drop by drop, before entering the pump.

We now take up the sixth group—a class of apparatus depending upon heat to separate carbonates and upon soda ash to eliminate gypsum. One of the best known purifiers of this type consists of a hot well, soda supply tank and filter. Returned steam and water, soda and raw water enter the apparatus at the top. Trays are here provided to thoroughly mix the water and steam. Carbon dioxide gas at once separates the carbonates and sulphites precipitate, and all fall into the settling chamber, spreading laterally under a cloth filter. About one-half hour after the raw water enters the apparatus it passes to the boiler. The soda solution is pumped by a small piston attached to the boiler feed pump and is therefore positive in its action.

Very large installations have been introduced with success.

Similar to this is the soda-grits purifier. Caustic soda or soda ash or both are pumped into a raw water line leading to a hot well under pressure. From here the water is drawn through a quartz filter of coarse mesh. Once a day the water is by-passed while the filter flow is reversed and the filters cleaned.

In the case of soda ash heat treatment the water must be at a minimum temperature of from 176–185° F., preferably 190–200° F.

ELECTROCHEMICAL TREATMENT.

Several years ago a concern leased a lantern-shaped basket of white metal balls to be used in boilers to prevent the formation of scale. Shortly after these appeared I analyzed one of the balls and found it to contain 40 per cent. zinc, with lead, copper, tin, antimony and bismuth. Not long afterward a patent was granted on this combination of metals.

A great many installations were made under guarantee to prevent the formation of scale. After several months a mushy shapeless mass with a small nucleus of metal would be found in place of the ball.

Recently one of the owners of this process discussed their experience with me. He stated that balls of certain composition could be applied only to peculiar kinds and types of water and that others of different metals would have no action.

A still more remarkable claim is that one set of balls will act for a few months. Disintegration of the metal then ceases and another set of different composition must be used.

The whole experiment proved very interesting but as far as I know no definite scientific facts have been accumulated.

CHEMICAL TREATMENT—INTERNAL.

When scale begins to collect in a boiler the engineer

employs a "boiler compound" so called. This is a generic term applied to any material added to water just before it enters the boiler or added to the boiler itself after cleaning and washing out. These compounds are found on the market both in a liquid and solid state. The methods employed in their sale by unscrupulous manufacturers have brought the business into disrepute. Such compounds have usually been gotten up by unscientific men who have been at their wits' end to prevent the formation of scale in the boilers under their charge. In many instances some by- or wasteproduct of the plant itself has been found to possess anti-scaling properties.

This is illustrated by the use of spent tan liquor which will, when added to boiler water even in small quantities, rot and honeycomb scale that has formed and will prevent the accumulation of new deposits. This is also true of sugar and starch wastes.

The boiler feed-water in isolated sawmills in the woods often proves to be absolutely free from scale-forming constituents. Many patents have been issued for these practical recipes and scientific men have investigated the materials and have found that anti-scaling properties are due to the presence of two or three fundamental bodies.

The first of these is tannic acid which is a constituent of many barks and is found in quantity in oak, hemlock, quebracho, catechu, logwood and sumach. The boiler compound vender who tells you that he has a purely vegetable material imported from China, India or Africa usually employs the bark or wood in a finely powdered state or the extract. Experiments have been made under widely differing circumstances proving conclusively that free tannic acid attacks iron. The barks and woods that are used contain this principle in the form of a glucoside less active. Tan-nate of soda is still less corrosive.

The second group of boiler compounds depends for its active properties upon caustic soda, soda ash or sesquicarbonate of soda. Sometimes we have found hydrate or carbonate of potash. The use of this class of materials is the result of long experience in the manufacture of soda and alkalis generally. Unless highly concentrated and under very high pressure these alkalis preserve metal instead of destroying it.

The history of the caustic soda industry shows that this compound was originally concentrated in ordinary steam boiler shells and that more difficulty was experienced in the caking of the concentrated salt about the stay-bolts and tubes than from any corrosive action.

One of the most amusing circumstances in connection with the use of these compounds is the steady and persistent objection of the engineers of many plants to the use of soda ash or caustic soda but they will use compounds, the basis of which is one of these materials.

Another class of really efficient boiler compounds includes phosphate of soda which has active softening properties both when applied to old scale and that newly formed; further a large class of special chemicals

has been found to have an active effect in connection with the removal or prevention of scale. Their expense often precludes their use.

The patent office reports present an interesting record of the progress of this rule-of-thumb business to an interesting, scientific and accurate apportioning of chemicals to a boiler water, the result of analytical data and experience, and I am often surprised at the variety of chemical materials pressed into the service for this purpose. More recently barium aluminate has been applied.

The only bar to the use of impossible and injurious combinations is the boiler inspector whose business it is to inquire carefully into the history of any solid or liquid used in a boiler. One of the most interesting compounds that has come to my attention is permutite. This is a sodium zeolite which removes carbonates and sulphates of lime, magnesium and iron. It may be revived by common salt and used again and again. We understand it is used outside the boiler as a filter and purifier.

CHEMICAL TREATMENT—EXTERNAL.

The chemist is now able to predict with considerable accuracy the kind of treatment that a water demands to make it available for power plant use. His formulas are, however, of but little value in a written report to the engineer. They are usually placed on file or unfavorably discussed in connection with similar communications that were received the year before.

Every power plant necessarily becomes a separate study as far as its water problems are concerned and it is to the advantage of all interested parties to have a running record month by month of the quality of the water received, whether it be from well, lake, river or city supply. Such data become of the greatest value when an important question relating to scaling, corrosion or fouling of tubes occurs.

The writer has a water-softening plant in operation where the source of supply is a creek. Sometimes this water is red on account of aniline dyes; at other times it carries iron salts from pickling vats. In one particular instance the odor from the plant became intolerable and it was found that seepage from a pea-vine silo was contaminating the supply. In every instance a change in the water was accompanied by an inquiry from the owner as to the reason.

Other instances might be cited substantiating the claim that I have made—that a full history of the water should always be available.

If the quality of water supplied to a plant is such that it cannot be used in boilers without chemical treatment the study should be taken up further and the total cost of plant operation in excess of that required were the water not purified made the subject of investigation. Cost of coal, gaskets, boiler tubes, washing out, power-hammers, loss of service of boiler, interest on the investment should be taken into account, and if a softening plant can be installed and the initial expense, cost of labor and materials are less than in the first instance a purifying plant certainly becomes a profitable investment.

The character of the water will largely determine

the kind of purification plant to be used. There are waters which can be taken care of splendidly with soda ash and filtration. These are high in gypsum and may contain some carbonates. Waters that contain 30 or 40 grains of carbonates per gallon can be treated inexpensively, accurately and successfully with lime.

Waters containing carbonates and sulphates require both a lime and soda ash treatment. To proportion these to the water, changing as it may from hour to hour, is a very difficult matter and only by using very large reservoirs and accurate measuring devices can an average treatment be applied. There are several excellent systems in the market.

There are waters that are saturated with gypsum or nearly so. I have found from 95-106 grains per gallon in five deep wells in or near Syracuse, N. Y. Such water cannot ordinarily be used for boiler purposes by any method of soda-lime softening. Please do not understand that it is impossible to remove the calcium and magnesium salts from this water: it can be done accurately and successfully in the cold to a point representing the limit of solubility of hydrate of magnesium and carbonate of calcium. But such water shows a constant tendency to foam so that it is unsafe to use the steam generated in an engine. However, one of my clients has successfully operated for four years a boiler in a limestone quarry where the water contains 93 grams of gypsum per gallon. Foaming is unknown.

FOAMING.

Water containing oil, a large amount of sulphate of soda or salt is often hard to handle in the boiler. It rolls and bounds and frightens the fireman. It may cause great damage to the engines. If returned oil has accumulated and made the water troublesome it should be removed and a good separator installed. If a separator is already in place it should be cleaned. Mineral salts are usually concentrated in the boiler many fold. At a certain stage of this accumulation the water will foam. The lime soda process ex-

changes sulphate of soda for sulphate of lime. This should be blown out at regular intervals. There is no reason why it should be allowed to accumulate in the boiler.

A complete and careful analysis of a sample of water from the boiler will usually indicate the cause of foaming and the remedy is easily applied. On the other hand incorrectly arranged feed pipes may lead to this difficulty, or the fireman himself may be entirely to blame for it has been said that a poor fireman can foam any boiler.

CORROSION.

Even though water does not scale boiler tubes it may corrode the metal, in which case it is much more dangerous than scale. Immediate action should be taken to locate the cause and provide a remedy. It is safe under such circumstances to make the feed water slightly alkaline with caustic soda or soda ash. I have received a sample of boiler sludge containing when dried out 60 per cent. oxide of iron, due to acid water in the boilers.

A manufacturer at Buffalo, N. Y., uses well water that is saturated with hydrogen sulphide. This is used for cooling purposes. It is piped about the plant in lead tubes and has so badly corroded a 12-in. I beam that this will have to be replaced. The cooling system fed by this water requires new piping annually. It is unnecessary to say that such a supply should never be used in any power plant. Many expensive and deep wells would become available if there were a simple and inexpensive method of removing sulphuretted hydrogen.

One of the most severe cases of corrosion brought to my attention was not cured by 10 pounds of zinc slabs per week but was stopped by blowing down the boilers often. The excessive use of tannin compounds in a horizontal return tubular boiler apparently resulted in a large number of pin-holes in the tubes. The accumulated scale was coal-black.

In one instance I have found severe corrosion of metal where the water is high in gypsum, low in

TABLE IV.—SHOWING METHODS OF PURIFYING BOILER WATERS IN TYPICAL NEW YORK STATE PLANTS.

H. P.	Total hardness.			Type of boiler.	Method of purification.
	Temp.	Perm.	Heater.		
125	1	4	Closed	Return tubular	Compounds
250	1	4	Closed, hot well	Water tube	Soda ash
2000	1	4	Closed	Return tubular	Soda ash
300	1	4	None	Return tubular	Boiler compounds
250	7	1	Closed	Return tubular	Caustic soda
4000	7	1	Closed	Water tube	No treatment
100	2	8	Closed	Return tubular	Soda ash
100	9	1	Closed	Return tubular	Caustic soda
600	6	8	Closed	Return tubular	Caustic soda
1000	4	10	Pressure hot well	Return tubular	Lime-soda plant
3150	7	8	Closed	Water tube	Turbine returns
500	15	..	Closed	Return tubular	Boiler compounds
600	15	..	Closed	Water tube	Boiler compounds
600	15	..	Closed	Water tube	Caustic soda
300	4	12	Closed	Return tubular	Soda and filter
4000	3	14	Closed	Water tube tubular	Soda and sand filter
4000	5	17	Closed	Water tube	Lime-soda plant
4000	5	17	Closed	Return tubular	Lime-soda "
200	11	15	Closed	Return tubular	Lime-soda "
2000	11	15	Closed	Return tubular	Lime-soda "
600	11	15	Closed	Return tubular	Tannates
100	5	80	Closed	Return tubular	Soda ash outside the boiler

organic matter and containing no chloride of calcium or magnesium.

This subject requires a large amount of scientific study.

SUMMARY.

Water containing not more than 3 grains of sulphates and carbonates per gallon can usually be treated by heat alone.

Waters of medium hardness may be treated within or without the boiler, preferably without. Very hard water requires chemical treatment in a well designed softening plant. Some waters cannot be treated economically and are useless for boiler purposes.

The returned water from a plant is soft and free from mineral matter. If oil is present it should be removed and the water used as many times as possible. If it corrodes the boiler one or more grains of alkali per gallon may prevent this action.

Condensed water from steam turbines and surface condensers is oil-free. This is an argument in favor of their use.

Lime is ideal as a water-purifying agent as it practically removes the carbonates of lime and magnesium—it should be free from magnesium oxide.

Any softening agent that leaves sulphate of soda in solution favors foaming. The ideal purification removes the sulphate entirely.

Monthly analyses should be made and kept on file of the water from the intake and from the boilers.

Blowing down-boilers will often save much labor and expense in the treatment and removal of tubes.

I wish to conclude this paper with a plea for more systematic investigation of the causes and prevention of scaling, corrosion, priming and foaming—conditions that present themselves in thousands of power houses annually.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY, No. 191.]

A NEW RAPID AND ACCURATE VOLUMETRIC METHOD FOR THE DETERMINATION OF MANGANESE AND ITS APPLICATION TO THE ANALYSIS OF IRON AND STEEL.

By F. J. METZGER AND L. E. MARRS.

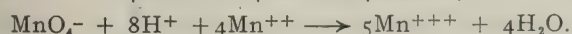
Received April 10, 1911.

It has been observed for some time¹ that the presence of manganese is a disturbing factor in the determination of ferrous iron in rock by the sulphuric-hydrofluoric acid method, and that the more hydrofluoric acid present, the greater the tendency to produce high results. This fact led to the supposition that in the presence of sufficient hydrofluoric acid, manganese and permanganic acid would react quantitatively, thus giving a method for the determination of the former.

Preliminary experiments proved that in the presence of sufficient hydrofluoric acid, the manganese, after the reaction, is all in the trivalent form; thus:



and $4\text{Mn}^{++} + 4^{(+)} \longrightarrow 4\text{Mn}^{+++}$, or



From this it is apparent that the value of the per-

¹ See Hillebrand, U. S. Geol. Survey, *Bull.* 422; "The Analysis of Silicate and Carbonate Rocks," pp. 162, 163.

manganate solution in terms of iron multiplied by 0.78682 (1911 atomic weights) gives the value in terms of manganese.

EXPERIMENTAL.

Solutions Used.—(1) Solution of potassium permanganate, approximately *N*/30; standardized against specially prepared Mohr's salt; 1 cc. = 0.001721 gram iron or 0.001354 gram manganese.

(2) A solution of manganous sulphate accurately standardized by precipitation as manganese ammonium phosphate and weighing as manganese pyrophosphate after ignition; 1 cc. = 0.002724 gram manganese.

Method.—Titrations were made in wax beakers, obtained by cutting off the tops of the ordinary white ceresine hydrofluoric acid bottles. A total volume of 100–150 cc. was used, containing 10 cc. sulphuric acid (1 : 2) and 25 cc. hydrofluoric acid. Measured volumes of the manganous sulphate solution were titrated in the presence of water, sulphuric and hydrofluoric acids with varying amounts of ammonium fluoride as follows:

No.	KMnO ₄ sol. used. cc.	Weight of ammon. fluoride present Grams.	Weight of Mn taken. Gram.	Weight of Mn found. Gram.	Error. Gram.
1.....	20.15	5	0.02724	0.02728	+0.00004
2.....	20.90	5	0.02833	0.02830	—0.00003
3.....	20.15	10	0.02724	0.02728	+0.00004
4.....	20.90	10	0.02833	0.02830	—0.00003

The endpoint is a distinct pink which lasts several minutes; the reaction proceeds somewhat slowly toward the end and the titration must be completed drop by drop. Sometimes there is a slight brown color at the end of the titration but the appearance of the pink end point is distinctly and easily seen. With amounts of manganese above about 40 mg., some experience is necessary for the recognition of the endpoint which is slightly masked by the brown color due to manganic salts. Ammonium fluoride increases the speed of the reaction but the effect of 10 grams is not sufficiently greater than that of 5 grams to justify the use of so much of the reagent.

Next, titrations were made similar to the above with varying amounts of ammonium fluoride and in the presence of 0.5 gram of iron (added in the form of ferric ammonium alum) in each titration. The results were as follows:

No.	KMnO ₄ sol. used. cc.	Weight of NH ₄ F present. Grams.	Weight of Fe ⁺⁺⁺ present. Gram.	Weight of Mn taken. Gram.	Wt. of Mn found. Gram.	Error. Gram.
5.....	20.2	1	0.5	0.02732	0.02735	+0.00003
6.....	20.2	2	0.5	0.02724	0.02735	+0.00011
7.....	20.18	3	0.5	0.02724	0.02732	+0.00008
8.....	20.27	4	0.5	0.02729	0.02745	+0.00016
9.....	20.35	5	0.5	0.02754	0.02755	+0.00001
10.....	20.55	6	0.5	0.02778	0.02772	—0.00006
11.....	20.31	7	0.5	0.02749	0.02750	+0.00001
12.....	22.55	8	0.5	0.03054	0.03053	—0.00001
13.....	20.75	10	0.5	0.02806	0.02810	+0.00004
Sum of 13.	267.46	—	—	0.36164	0.36203	+0.00039

It is seen that the presence of ferric iron does not affect the accuracy of the method. One gram of ammonium fluoride completely decolorizes 0.5 gram of

ferric iron; the same effect can be obtained by using 2 grams of potassium or sodium fluoride, but as these dissolve with difficulty, the readily soluble ammonium fluoride is to be preferred.

From the sum of titrations 1-13, 267.46 cc. of the permanganate solution is equivalent to 0.36164 gram manganese or 1 cc. $\text{KMnO}_4 = 0.001352$ gram Mn, which is in very good agreement with the value obtained by calculation from the iron standard of the permanganate.

The great accuracy of the above method is apparent when we consider the low equivalent of the permanganate solution in terms of manganese, together with the fact that the end-point is very easily obtained within one drop of the permanganate solution.

The Analysis of Steel.—Weigh out about 1 gram of sample; dissolve in 10 cc. of nitric acid (1 : 1) in a covered casserole. Cool slightly; add 1 gram of ammonium persulphate and let stand until effervescence ceases; boil briskly for a few seconds, remove cover and evaporate to dryness (do not bake); take up with 20 cc. of sulphuric acid (1 : 2) and 30 cc. of water and boil until the solution is clear. Cool, transfer to a wax beaker, add 5 grams of ammonium fluoride, 25 cc. hydrofluoric acid, dilute with water to a volume of 100-150 cc. and titrate. The solution is colorless and the pink endpoint is very easily seen. As much as 2 cc. of concentrated nitric acid has no effect on the titration; hence, if the residue has become baked add 1 or 2 cc. of dilute nitric acid to make complete solution take place readily.

The above method was applied to twelve samples of steel purchased from the Bureau of Standards, Washington, D. C. The results are given here in tabular form.

No.	Bureau of Standards, Mn, per cent.			Found, Mn, per cent.		Average.	Difference between authors' and B. of S's avgs.
	Low.	High.	Average.				
14 Bessemer 0.1 C.....	0.485	0.552	0.513	0.545	0.547	0.546	+0.033
15 Acid open-hearth 0.1 C.....	0.388	0.440	0.412	0.413	0.438	0.425	+0.013
16 Basic open-hearth 0.1 C.....	0.506	0.560	0.528	0.519	0.538	0.529	+0.001
17 Bessemer 0.2 C.....	0.866	0.911	0.890	0.946	0.961	0.953	+0.063
18 Acid open-hearth 0.2 C.....	0.726	0.800	0.760	0.795	0.806	0.800	+0.040
19 Basic open-hearth 0.2 C.....	0.436	0.520	0.464	0.513	0.515	0.514	+0.050
20 Bessemer 0.4 C.....	0.835	0.924	0.872	0.934	0.940	0.937	+0.065
21 Acid open-hearth 0.4 C.....	0.460	0.520	0.486	0.533	0.540	0.537	+0.051
22 Basic open-hearth 0.4 C.....	0.376	0.443	0.406	0.442	0.443	0.442	+0.036
23 Basic open-hearth 0.6 C.....	0.524	0.620	0.568	0.588	0.599	0.593	+0.025
24 Basic open-hearth 0.8 C.....	0.626	0.703	0.654	0.688	0.689	0.688	+0.034
25 Basic open-hearth 1.0 C.....	0.320	0.460	0.405	0.465	0.472	0.468	+0.053
Average.....							+0.037

The results obtained average 0.037 per cent. higher than the Bureau of Standards' averages and 0.002 per cent. lower than their highest determinations. Nine separate determinations are given for each steel in the Bureau of Standards' certificates, with an average variation of 0.076 per cent. and a maximum variation of 0.14 per cent. The authors' greatest variation in duplicates is 0.025 per cent.

The authors' results are uniformly slightly higher than the *average* results published by the Bureau of Standards, while they are almost identical (—0.002 per cent.) with the *highest* results, and on this account we wish to call attention to the fact that in the method described there are neither precipitations nor filtrations

and therefore no possible chances for loss of manganese, whereas, in other methods there are both precipitations and filtrations which might result in a small loss of manganese.

It is, of course, necessary that no carbon compounds exist in solution when titration is made, and the above treatment with ammonium persulphate in nitric acid solution insures their complete removal. Several other methods were employed to remove carbon compounds; namely, nitric acid alone, nitric and sulphuric acids, and ammonium persulphate in sulphuric acid, but none of these gave satisfactory results with all of the twelve samples given in the above table.

Duplicate analyses were made of each of the twelve steels by simply dissolving in nitric acid, evaporating to dryness, taking up in dilute sulphuric acid, then adding ammonium fluoride and hydrofluoric acid, and titrating as usual. Although the duplicates in all cases agreed very well, they were all slightly high, the average of the thirteen samples being 0.111 per cent. higher than the average of the results reported by the Bureau of Standards. Our results showed further that this procedure will give accurate results if, instead of calculating the value of the permanganate from an iron standard, the permanganate is standardized against a steel made by the same process and of known manganese content.

Analysis of Pig Iron.—Proceed as in steels: the combined carbon is all oxidized; the graphitic carbon is entirely without effect on the permanganate and can be left in the solution as it obscures the endpoint only very slightly. If the graphite is large in amount and its removal is desirable, the solution is filtered just before adding the ammonium fluoride and hydro-

fluoric acid. Results obtained with two Bureau of Standards' irons are given below.

Sample.	B. of S., Mn, per cent.			Found, Mn, Per cent.	Variation from B. of S., per cent.
	Low.	High.	Ave.		
C.....	0.62	0.68	0.66	0.727 ¹ 0.673 0.683 0.678	
				Average, 0.690	+0.030
D.....	1.38	1.43	1.41	1.49 ¹ 1.49 ¹ 1.52 1.48	
				Average, 1.495	+0.085

¹ Graphite not removed by filtration.

The method possesses all the advantages of simplicity, ease of manipulation, rapidity and accuracy. Fourteen of the analyses included in the above tables were made, complete, in one afternoon.

There are no precipitations or filtrations (unless it is desired to filter off the graphite from pig iron) and therefore no possible chances for loss of manganese during the process of analysis.

The method is now being applied to the analysis of spiegels, rock, manganese ores, etc., and we hope to report on these in this journal in the near future.

QUANTITATIVE LABORATORIES,
HAVEMEYER HALL,
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[CONTRIBUTION FROM THE TEXAS AGRICULTURAL EXPERIMENT STATION]

EFFECT OF IGNITION ON SOLUBILITY OF SOIL PHOSPHATES.

By G. S. FRAPS

Received February, 24, 1911.

It is known that ignition of the soil increases the quantity of phosphoric acid dissolved therefrom by acid. Stewart¹ uses this as a method for estimating the organic phosphoric acid of the soil. He extracts the original soil and the ignited soil with 12 per cent. hydrochloric acid, and assumes that the increased quantity of phosphoric acid secured originates from organic phosphates.

The object of the work here reported was to study the effect of ignition upon mineral phosphates such as may occur in the soil.

Method of Work.—The quantity of phosphate containing 0.1 gram phosphoric acid was weighed into a platinum dish and ignited for ten minutes, at a low red heat. It was transferred, dish and all, to a bottle, 200 cc. of 12 per cent. hydrochloric acid added, allowed to stand 24 hours, filtered, washed with hot water, and made up to 500 cc. Phosphoric acid was then determined in 200 cc.

Another series of experiments was made, in which the ignited phosphate was digested 5 hours at 40° with 500 cc. of *N*/5 nitric acid.

RESULTS.

The results of the experiments are reported in the table. Ignition increased the solubility of the phosphoric acid of these phosphates decidedly. With fifth-normal nitric acid, about ten times as much phosphoric acid is dissolved from the ignited phosphates, as from those not ignited. With the strong acid, ignition rendered practically completely soluble all the phosphates which were not already completely soluble in this solvent.

It is evident that no analytical method for organic phosphoric acid can be based on ignition. If the strong acid dissolves all inorganic phosphates, then any method which determines the remaining phosphoric acid will determine the organic phosphoric acid. If the strong acid does not dissolve all the inorganic phosphates (and we have evidence that it does not) then the remaining inorganic phosphates will be ren-

dered partly soluble in the acid by the ignition, so that the ignition method would not be accurate.

PHOSPHORIC ACID DISSOLVED FROM FIFTEEN SOILS AND ONE MINERAL
(In Percentage of the Quantity of Phosphoric Acid Used.)

Laboratory number.	With 12 per cent. hydrochloric acid.		With <i>N</i> /5 nitric acid.	
	Original mineral.	Ignited mineral.	Original mineral.	Ignited mineral.
240 Wavellite.....	...	100	4.8	80.7
721 Wavellite.....	19	100	4.5	97.5
726 Wavellite.....	18	100	2.0	58.0
714 Dufrenite.....	100	100	4.8	35.5
718 Dufrenite.....	86	96	8.0	75.0
716 Variscite.....	26	100	12.0	100.0
724 Triplite.....	100	100		

Phosphoric acid is not the only constituent of the soil whose solubility in acid is increased by ignition. We have examined twenty-five soils, and ignition increases the oxide of iron and alumina dissolved by the acid from every one of them. The increase is great in some instances. For example, in soil 3368, ignition increased the acid-soluble oxide of iron and alumina from 2.63 to 8.48 per cent., and in soil 1361, from 1.25 to 6.50 per cent. Full details of this work will be published in *Bull.* 135 of the Texas Experiment Station.

SUMMARY AND CONCLUSIONS.

1. Ignition increases about ten times the solubility of the phosphoric acid of wavellite, dufrenite and variscite in fifth-normal nitric acid.
2. Ignition renders variscite, dufrenite and wavellite almost completely soluble in 12 per cent. hydrochloric acid.
3. Ignition of the soil will probably render inorganic phosphates soluble in acid, and therefore is not a method for estimating organic phosphoric acid.
4. Ignition of the soil renders considerable quantities of iron and aluminium oxides soluble in acid.

COLLEGE STATION, TEXAS.
February 15, 1911.

DEVELOPMENT OF THE SUGAR INDUSTRY.¹

By AUGUST VON WACHTEL.

Received April 26, 1911.

The sketch submitted to your kind attention treats an extensive subject and necessarily will give only a general impression and not one adequate to the importance and the technical development of the manufacture.

The sugar industry was the pioneer in vacuum boiling a rational extraction of raw products by cheap evaporation and filtration, and solved first the problem of handling a difficult crystallization on the largest scale and in an entirely modern way.

Still this industry has the reputation of not being strictly a chemical manufacture—a wrong impression, as it must be either classified with logwood or tannin extractions where the methods of sugar manufacture are simply copied, or it can be compared with the manufacture of cream of tartar or alkaloids, which are all extracted from some natural raw material and a nearly chemically pure product turned out.

¹ Read before the New York Section of the Society of Chemical Industry, March 17, 1911.

¹ *Bull.* 145, Illinois Experiment Station.

The only difference is in general the gigantic scale of the business which requires perfect mechanical and banking facilities. The manufacture includes perhaps the largest individual plants of the chemical industry when results are considered in money. In the United States there are single refineries whose yearly output exceeds fifty million dollars worth of white sugar. In cane extraction the huge Chaparra or the Caracas in Cuba grind more than three thousand tons of cane daily in the season of six months, and all kinds of apparatus handling big masses cheaply are utilized in the numerous branches of the chemical industry.

Of the plants that produce cane sugar two are of primary importance and two of much inferior value *viz.*, 1st, Sugar Cane *Sacharum Officinarum*; 2nd, Sugar Beet *Cyca*, 3rd, Sugar Palm *Phoenix Sylvestris*; 4th, Sugar Maple *Acer Sachariferum*.

Total production of cane annually	9,000,000 tons.
Total production of beet annually	8,000,000 tons.
Total production of sugar palm annually	150,000 tons.
Total production of maple sugar annually	500,000 tons.

Cane sugar is widely distributed in nature, as in the strawberry, raspberry, apples, pineapples, water-melons, etc., but the raw product is too expensive and the yield too small.

The sugar cane is a native of Bengal according to Decandolle and is nowhere found in the original state.

The sugar palm and maple are wild trees and not cultivated and the sugar beet is yet found in a wild state on the shores of the Mediterranean.

The first mention of sugar in crystallized form is made about 800 B. C. It was known to the Romans only as sugar plant, but in 800 A. D. we find in a list of presents made by Harun al Rashid to Charlemagne, some sugar, snow-white, in conical form (loafs), ringing like a bell and made from sugar cane. It was surely well refined sugar to have such properties and vindicates the highest standing of civilization in the Arabian Khalifate. The Crusaders brought home an extended knowledge of sugar, coffee, tea and other tropical products and introduced their use into Europe. For hundreds of years Venice controlled the land passage to East India and the Sea routes from Asia Minor and distributed their goods all over Europe at such fabulous profits as to make it the center of the world's trade and the Queen of the Seas for nearly 600 years.

In 1420 Venice acquired the secret of sugar-refining and on this monopoly collected a high toll from all the known world. But already storms were gathering. With the discovery of the magnetic needle the enterprise and courage of the maritime nations made quick progress.

Spain discovered the Canary Islands, The Portuguese the Cape Verde Islands and the Azores. At the same time they sailed around the Coast of Africa beyond the Equator and established everywhere plantations of sugar, coffee, pepper, and all tropical products so successfully that they undersold Venice, ruined her trade and made Lisbon the new emporium of trade for nearly a century.

The first cane sugar was produced by European

around 1400 A. D. As a last blow to Venice the Turks conquered Constantinople in 1453, and destroyed all caravan roads from East India beyond hope of recovery.

In the last decennium of the Fifteenth Century two momentous events changed all conditions of the European world—the discovery of America and the landing of Vasco de Gama in Calcutta by sea from Lisbon, and shortly afterwards the discovery of the Pacific Ocean and the circumnavigation of the World by Magellan. Spain's dominant position shifted the center of trade from Lisbon to Antwerp—then a Spanish possession—for another century and finally on Amsterdam and London, after the downfall of the Armada and the end of the Spanish supremacy on the seas.

The first black slaves were introduced from Africa in 1662 into the Barbadoes by English sugar planters, and the institution of slavery was established from that time in all newly discovered countries as the legal labor supply.

The price of sugar when monopolized by Venice in 1420 was \$2.70 per pound and 50 cents in 1520, and fell continually until the present day when it is produced so cheap that we may call it bottom prices.

London quotations.		Prices of sugar per pound.
1700	1710	32.24
	1720	29.76
	1730	...
	1740	14.91
	1750	10.92
	1760	19.40
	1770	...
	1780	20.96
	1790	13.44
	1800	18.34
	1810	11.77
	1820	8.66
	1830	5.87
	1840	11.79
	1850	6.25
	1860	6.80
	1870	5.35
	1880	4.42
	1890	3.69
	1900	3.16

The prices are not quite comparable as the money value was higher and the quality of sugar lower.

The fluctuation of sugar prices is often enormous as may be judged from the recent London quotations. It is due to three factors: (1) crop results, (2) constantly increasing consumption, (3) constantly increasing production in the world.

	Per pound.
October, 1909.....	\$2.64
May, 1910.....	3.62
October, 1910.....	1.99
January, 1911.....	2.25

The cane plant was regarded as the sole source of sugar until a scientific discovery of Markgraf in Berlin in 1745, which showed a crystalline sugar present in the beet and other plants. About forty years later the discovery was put to a practical test by Frank K. Achard, the son of a French Huguenot refugee, who erected a small plant in Silesia, Prussia, for the purpose of exploiting the discovery of Markgraf, and had some success with it. Shortly after, Napoleon, anxious to replace cane sugar, a foreign product coming over the sea, and to deal England a blow, encouraged the new

manufacture by offering money for the erection of beet sugar factories in France. Calling on such an establishment near Paris in 1810, he ordered ten new factories built at once, regardless of cost. Through his protection the beet industry was put on such a solid basis at one stroke that it withstood the effects of subsequent improvements and increased competition of cane sugar. Napoleon is justly credited as the practical founder of this gigantic industry, which by 1865 supplied the total European Continent with beet sugar alone. The identity between cane and beet sugar was finally established by Biot's discovery of the circumpolarization of light in 1830.

The *modus operandi* of cane sugar manufacture as practiced one hundred years ago was first to press the cane in roller mills and to extract the juice, which was then clarified by boiling with a little lime (about $\frac{2}{3}$ per cent.), and the reasonably clear juice siphoned off and evaporated in iron kettles over free fire. The properly thickened juice was cooled in iron or wooden tanks and stirred to help crystallization. The crystals were separated from the sirup in barrels with a false bottom. In working the beets, the principles of cane manufacture were first adopted. The beet was grated to a mush and the juice pressed with powerful hydraulic presses, and then clarified, as with cane, with a small quantity of lime and boiling. The subsequent working was by steam evaporation, the vacuum pan purifying the crystals in loaf form.

Technical progress in the 19th century created a new manufacture by a series of inventions which must be recorded:

1815. Howard invented and introduced the vacuum pan.

1822. Figuier discovered the decoloring action of bone-black.

1830. Derosne showed how to revivify bone-black so that it may be used over again many times.

The greatest progress and the establishment of the present modern manufacture dates from the sixties and seventies of the former century and from the following improvements:

(1) The invention of the diffusion process for the beets in Seelowitz, Austria, by Florent and Jules Robert, natives of France. The process is the first perfect attempt to extract soluble materials without much dilution. The beet was cut to slices and exhausted without destroying the cells. A regular diffusion was effected in which the yield of juice was greater, and the quality superior to anything known before. There is no other process practiced to-day in the beet sugar manufacture.

(2) The introduction of Jellinek saturation. Jellinek, a native of Bohemia, in Austria, was not satisfied with the old mode of clarification, and devised a new and better plan by mixing the juice with a large amount of caustic lime (about 2 per cent.), which he precipitated with carbon dioxide gas made in specially constructed kilns. The lime was burned with coke and the gases of combustion containing all the carbon dioxide gas from the lime and coke were obtained. The carbon dioxide gas was in this way enriched to

about 35 per cent. in volume, and was amply sufficient in quantity to precipitate all the caustic lime as a carbonate, and occluded in the precipitation all mechanical and many chemical impurities. There was yet one difficulty to overcome—to master the accumulating copious precipitation of lime carbonate. This was solved by Jellinek, by the inventions of the filter press, first constructed by the famous Danek machine factory. With slight variations the filter press has been introduced in numerous other industries with great satisfaction.

(3) By the invention of the multiple effects of Rillieux, a Louisianian, whose invention was developed by the help of Florent Robert in Seelowitz, Austria, to make a practical success. Robert's multiple effect had an upright form, and the present prevailing horizontal form dates from the seventies by Wellner Jellinek, from Austria where it was first employed.

(4) A modest, but nevertheless very important improvement was the introduction of the beet flume, a cemented water gutter with sufficient fall to float the beets into the factory from the bins or yards, thus saving greatly on hand labor. It is used in all beet factories without exception, and in many instances it is adapted to float cane for long distances, especially in the Sandwich Islands. The invention was made by Reidinger, a Hungarian.

(5) The Centrifugal, a Scotch invention which separates the crystals from the massecuite or fill masse, the thick mush coming from the vacuum pan, which contains the crystals mixed with sirup, the so-called hanging centrifugals exclusively used in the United States, is Hepworth's invention. The American Tool and Machine Company produces the hanging Weston centrifugal, best known in America. All beet sugar factories work on the same plan the world over, and only minor improvements have been added after the seventies, *viz.*, the Omose and other process to regain sugar from molasses, the economical drying of beet pulp, making it a cattle food that keeps well, and finally the crystallization in motion, completing the cycle. There is little to improve in beet sugar in our present knowledge.

The cane sugar manufacture adopted all the foregoing improvements suitable for it: the multiple effects, vacuum pan, filter press centrifugals. The method of clarifying is essentially the old one. The greatest stress is justly laid on the extraction of the juice by employing the most powerful roller mills in sets of three rolls, which results are factories with six, nine, and twelve to fifteen rollers. Nine roller mills are mostly used, the pressure gradually rising to about 400 tons in the last set of rollers. A so-called crusher goes ahead of them.

On account of the peculiar form of sugar cane the problem is very difficult and the extraction of the juice is still waiting for a better solution. The bagasse or pressed-out cane containing the fiber is dry enough to burn and constitutes the fuel for the manufacture. It is sufficient to give all the steam required.

A great part of the financial success of the beet

sugar in competition with cane is due to the improvement of the quality of the beet by Vilmorin, in Vincennes. Vilmorin argued that in manufacturing sugar we only extract it, and the beet field is the true laboratory of sugar-making. To get a higher yield we must raise beets with a higher percentage of sugar.

The manner in which he accomplished his purpose was by raising beet seed from beets, showing the highest sugar content. The best formed beets with the highest specific gravity having been selected, he took from each beet small samples in the form of a cylinder with special apparatus and with a delicate scientific outfit of his own invention, he analyzed 5 cc. of the juice. The best beets in sugar content and purity were used for next year's propagation. In the course of a life's effort he increased the average of sugar from 12-18 per cent. and laid the foundation for the high yield in sugar of the present day, now averaging 13-15 per cent. All leading beet-seed raisers without exception follow the above system in Germany, Austria and France, Russia and Belgium. The analysis is invariably made by girls, and thousands of them are employed in a single establishment during the season.

The greatest advance in raising the cane plant was made lately in the Barbadoes agricultural station. At all times cane was propagated by ratoons, or pieces of cane stalk or tops buried in the ground to make the eyes sprout. Botanically it is analogous to the well-known propagation of wild oats. A sexual propagation was tried for centuries and was thought wholly impossible; in spite of the blossoms present on ripe cane containing the male and female parts no fertilization took place. It was effected only by planting different varieties of cane side by side. According to this mode of fertilization every plant so obtained was a hybrid and different from each other. Of these the best varieties were selected, and in time may prove to be a valuable improvement in producing cane with different properties.

Refining.—By refining is understood producing pure white sugar from a yellow raw sugar, as it comes from beet or cane. The beet sugar especially has a dirty obnoxious odor, and its use in the raw state is impossible. The bulk of beet and cane sugar are so-called centrifugals, produced by boiling in vacuum to a large grain polarizing 94-97 per cent. (with 2 per cent. water) and centrifuged. In refining, the sugar is dissolved in water about half and half to save in evaporation, filtered mechanically next over bone-black to take out impurities. It is finally boiled in vacuum and centrifuged to fine granulated and dried in the United States. You all know the product.

In Europe very fine loaf sugar, and in some parts very coarse lump sugar, is in use, both of which are more expensive to manufacture than granulated, and consequently are higher in price—especially the fine loaf sugar. In this country three-quarters of the sugar is in the barrel in three days after dissolving. For fine loaf sugar it takes three weeks. A refinery in Europe is much larger for the same output and requires more capital than in America. The refined

sugar is dearer. The loaf sugar dissolves much quicker than granulated—a quality demanded by the public taste. The crush or lump sugar looking like coarse sand cemented with a glassy mass dissolves as slowly as possible, as required by the mode of drinking common beverages like tea and coffee.

STATISTICS AND DUTIES.

Production in thousands of tons.	1885/6.	1907/8.	1908/9.	1909/10.	1909/11.	Estimated.
Beet.....	2,865	6,562	6,453	6,138	7,900	
Cane.....	3,184	4,534	5,123	5,825	5,800	

In these figures, as issued by mercantile papers, sugar-producing countries are not considered whose production is entirely consumed at home and are immaterial as far as market prices are concerned, *viz.*, East India and Louisiana.

PRODUCTION OF SUGAR IN 1000 TONS AROUND 1908/9.

Cane.		Beet.	
East India.....	3,500	Germany.....	2,223
Cuba.....	1,513	Austria.....	1,409
Java.....	1,241	Russia.....	1,403
United States, Louisiana.			
Sandwich Islands, Porto Rico and Philippines.....	100	France.....	719
China and Formosa.....	250	United States.....	300
All English Colonies with Egypt.....	642	Belgium.....	235
Spanish America.....	603	Holland.....	173
French Colonies.....	105	Italy.....	150
		Sweden.....	109
	8,954	Spain.....	106
		All other countries.....	85
			6,972

Until 1878 France was the leading beet producer. Then she yielded the field first to Austria, and next to Germany, which for a generation has been the biggest factor in the beet production of the world. The largest increase recorded was made last year in Russia, which in all probability will be the banner country for the future.

It would lead too far to explain the cause of the changes, which is mainly a question of adaptable land and consumption, much depending on duties and internal revenue.

YEARLY CONSUMPTION PER CAPITA IN POUNDS.

1910.			
England.....	93.50	Germany.....	40.92
United States.....	83.00	France.....	36.08
Denmark.....	73.68	Belgium.....	29.70
Canada.....	72.00	Austria.....	24.32
Switzerland.....	55.22	Russia.....	20.55
Sweden and Norway....	47.88	Spain.....	11.37
Holland.....	41.40	Italy.....	7.83

DUTIES AND INTERNAL REVENUE.

United States Duties.

For raw sugar polarizing, 75 per cent....	\$ 0.95 cents per pound
For every per cent. in addition.....	00.035 cent per 100 pounds
All above.....	1.90 per pound

Sugar of 95 per cent. polarization pays a duty of \$1.65, and when foreign sugar is worth \$2.25 in the United States, the home producer of cane or beets receives \$3.90 for his product.

England.....	45.5 <i>ad valorem</i> .
Russia.....	8.8 per pound internal revenue.
Spain.....	7.7 per pound internal revenue.
Italy.....	10.5 per pound internal revenue.
Germany (recent law).....	1.5 per pound internal revenue.

Generally speaking the cheaper the sugar the greater the consumption. The northern people consume more sugar than in the southern climes, richer nations more than poorer, and in prosperous business years the consumption increases and decreases in bad years. The per capita consumption increases constantly in all countries of the world.

COMPARATIVE COST OF PRODUCTION IN CANE AND BEET.			
Cane.		Beet.	
Cane produced at \$2.00 per ton, required for one ton of sugar, 10 tons.		Beet produced at \$3.50 per ton, required for one ton of beet, 7 tons.	
Cost of cane per one ton of sugar.....		Cost of beet per one ton of sugar.....	
\$20.00		\$24.50	
Fuel only for starting and after interruptions.....		Fuel one ton.....	
\$ 1.00		\$ 4.00	
Other expenses.....		Other expenses.....	
\$10.00		\$10.00	
\$31.00		\$38.50	

OTHER CONSIDERATIONS NOT LISTED OR CALCULATED	
Length of Campaign	
Cane.	Beet.
150-180 days	80-100 days
Character of Soil	
Almost any rich soil.	A special light, rich and deep soil.
Storing	
No storage, worked directly from field.	Must be carefully stored.
When Left in the Field by Impossibility of Hauling	
Cane will grow that much larger.	Beet is a total loss.
Labor	
Often insufficient in quantity and quality.	Mostly excellent and sufficient.
Mostly reliable.	Mostly stable.
Government	
In far away countries.	Close at hand—home consumption
Communication	
Unsatisfactory.	Excellent as a rule.
Canefires	
Hurricanes, earthquakes and other incalculable drawbacks.	None.

PLANTS AND MACHINERY

SUPERHEATED STEAM IN INDUSTRIAL PLANTS.

By ROBERT H. WYLD.

The use of superheated steam for economizing steam and fuel has only become general within the past few years. Its value has now been proved and it is now being utilized to an ever-increasing extent for a great many purposes.

Its use may be divided into two distinct classes of work: first, for increasing the economy of engines, turbines and pumps in connection with the generation of steam power, and second, its use in various industrial processes where heat is required for boiling, cooking, distilling, drying or similar operations.

The value of superheated steam for increasing the economy of steam engines has been known for a great many years and it was taken advantage of in the early days in connection with the simple engine then in use operating on low steam pressures. As steam pressures were increased lubrication difficulties were experienced, due to the fact that the lubricants used in those days were not suited to high temperatures, and this was also true in regard to the earlier forms of piston rod packing, gaskets and the free use of babbit metal then in vogue. Some of the general features of engine design for low pressure steam conditions, such as valve design, also acted to retard the use of superheated steam. At the present time, however, all these difficulties have been overcome. Good cheap mineral oils are easily obtained as well as suitable packing, gaskets, etc., and as a result superheated steam is rapidly coming into general use in the power plant.

In these days the average manufacturer or central power station operator is tremendously interested in any apparatus that will reduce fuel bills and superheated steam will effect a considerable saving even in the most economical plant.

Generally speaking, superheated steam in the power plant will effect a saving in three ways: by the doing away with condensation in pipe lines, by eliminating cylinder condensation in engine cylinders, and by the

reduction of friction of the steam in the ports while entering and leaving the engine cylinder. The percentage of saving depends upon the design of the piping and whether the distance the steam has to travel is long or short, and also upon the economy of the engine or pump in which it is to be used. If it is found necessary to carry steam long distances, superheated steam is of especial value, as absolutely dry and superheated steam can be delivered at the end of very long lines. Its value is even greater in such cases if the steam lines are especially designed for its use. When superheated steam is used much smaller piping can be installed than would be possible with saturated steam, as the steam can be carried through the pipe at a much higher velocity without increasing the drop in pressure due to decreased friction losses in the line. Loss of pressure in a pipe is caused by condensation and by friction and with superheated steam the condensation loss is entirely eliminated and the friction loss is greatly reduced. In existing long lines it will be found that the steam pressure obtained at the end of the pipe will be considerably higher when superheat is in use. An interesting illustration of this is found at one of the plants of the U. S. Steel Corporation where nine pounds higher pressure is obtained at the end of a twelve-hundred-foot line of pipe when the steam is superheated.

Another case reported by a large Canadian concern is that after the installation of superheaters in their plant the pressure at the end of an eight-hundred-foot line of piping was found to be eighty pounds instead of sixty as formerly with saturated steam.

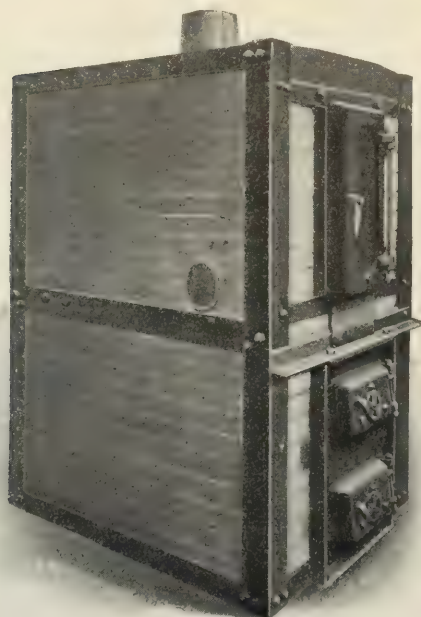
The average steam saving obtained by eliminating cylinder condensation in engines and pumps is about as follows: In triple expansion engines the saving will amount to about twelve per cent., in compound engines 14 per cent. and in simple engines 18 per cent. or more. In the case of slow-speed simple engines and direct-acting steam pumps the steam saving is often remarkably large, sometimes as much as forty per cent.

The fuel saving is not always in theoretical proportion to the steam saving and is usually somewhat less, in most cases amounting to about 6 per cent. in the case of triple expansion engines, up to sometimes as high as 25 or even 30 per cent. in the case of plants containing only simple engines and direct-acting pumps. In many cases, however, the equipping of a boiler plant with superheaters will increase the efficiency of the boiler as a complete unit, including furnace and superheater, and this increase of efficiency may be enough to compensate for the extra heat demanded to do the superheating or may even do more than this so as to make the fuel saving even greater than the steam saving. Results of this kind have been published as the results obtained by actual tests.

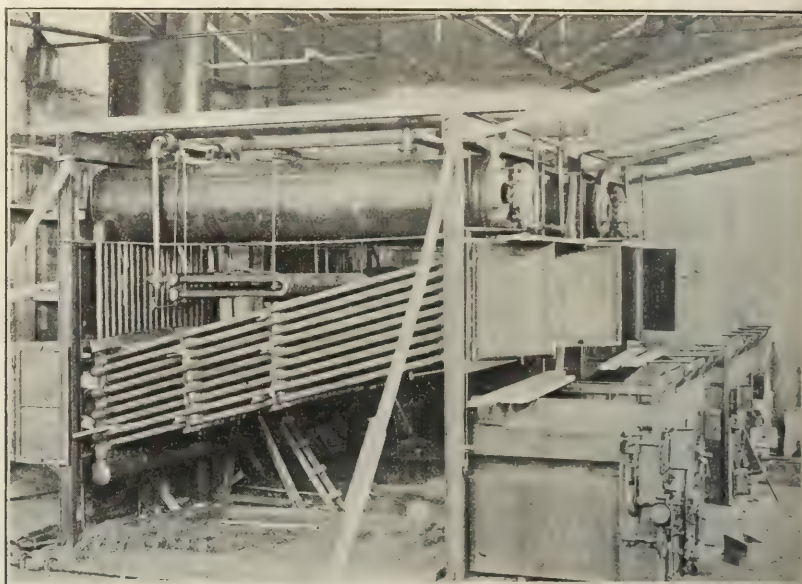
Superheated steam is of especial value in connection with steam turbines, for in this case not only a considerable steam and fuel saving is obtained, but

heated steam in such existing plants may be of great value. Instead of effecting a saving in fuel and steam a superheater installation may be made to increase the capacity of an existing boiler plant for work and it has been found that in an average plant, six boilers, equipped with superheaters will do the same work as seven without. Where boiler plants are overloaded and it is a difficult matter to add additional boilers, either due to restricted space or some other reason, the installation of superheaters will effect the same result and without any increase to the fuel consumption.

Some of the most interesting applications of superheated steam have been those where it has been used for industrial processes and new uses are continually being found for it. It may be used to advantage in almost any process where heat is required either for boiling, cooking, distilling, drying or similar work. Its substitution where the use of an open fire has been



Small direct fired superheater.



Superheater in horizontal water tube boiler.

absolutely dry steam is of advantage, due to the fact that water friction on the turbine blading is done away with and the life and capacity of the turbine thereby increased.

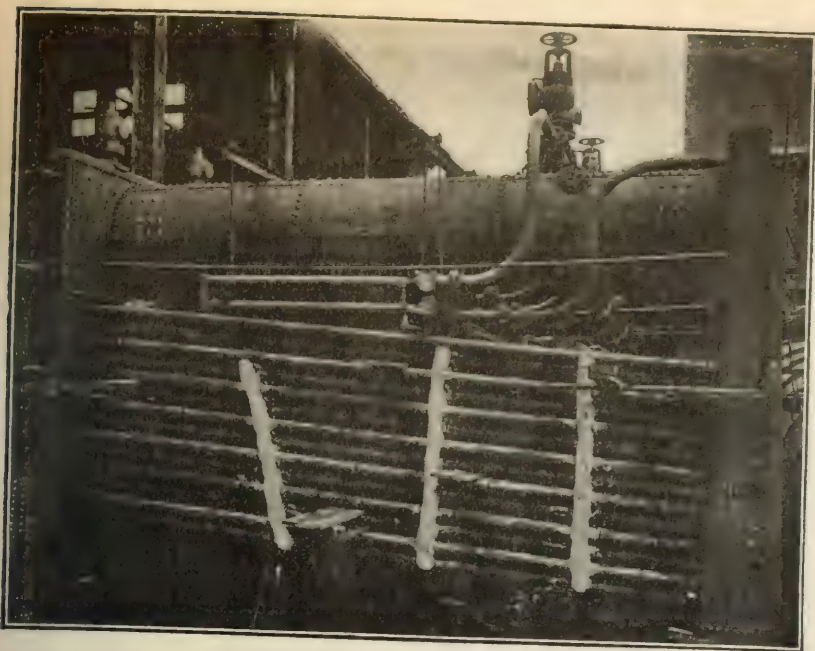
In connection with the above estimated savings it may be stated that these are figured on the basis of a moderate amount of superheat, with a final temperature of not more than 500° F. at the engines, corresponding to from 100° to 150° of superheat at the pressures generally carried. In American practice, higher temperatures are seldom employed, as such would require specially designed engines. With these moderate temperatures, however, very considerable economies can be obtained in the average plant and superheated steam in this way can be used in a plant already in operation without any material change in equipment, and it may be said that many such existing plants offer the greatest field for such economies.

Viewed from another standpoint, the use of super-

found necessary in order to obtain temperatures not obtainable by the use of saturated steam at ordinary pressures is a very interesting application. The fact that by superheating any reasonable temperature can be obtained regardless of pressure makes it possible to utilize it in ways where a direct fire was the only way to obtain the necessary results before its introduction. Superheaters are in successful operation supplying steam at temperatures as high as 1200° F. at the present time. Of course, in such cases the superheater has to be especially designed to withstand the heat, and superheaters constructed of bare pipe or tubing will not last under such severe usage. Mention of these special uses of superheated steam might be made.

GLYCERINE STILLS.

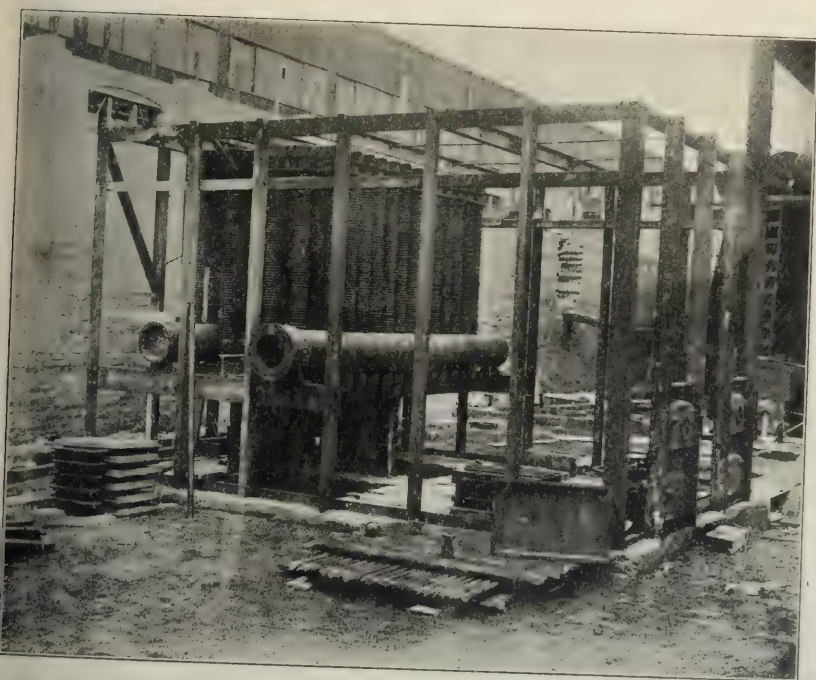
One interesting application is in soap works where it is desired to obtain high temperatures in glycerine stills. In one plant this result is reached by super-



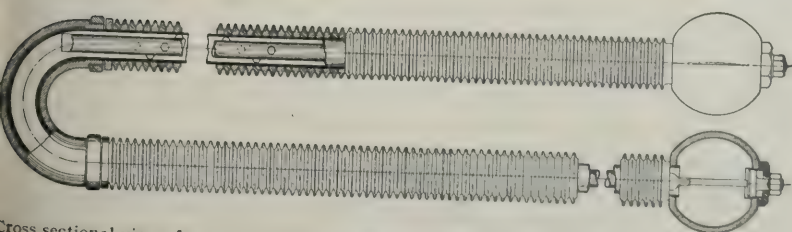
Superheater in horizontal water tube boiler.



Portable superheater, casing removed.



Direct fired superheater, before placing of brickwork.



Cross sectional view of return bend element and connecting headers used in the construction of superheaters."



Portable superheater.

heating steam in one of the boilers up to a temperature of somewhat over 600° F. The pressure maintained in this boiler is somewhat higher than in the others in the plant. The steam from this high pressure boiler is then passed through the coils of the glycerine still, leaving the coils in a still superheated condition and passing into the boilers at the lower pressure where it mixes with the rest of the steam. In this manner a temperature of 500° to 550° F. is easily maintained in the still.

In the lower pressure boilers the steam is again superheated and used for boiling soap and for power purposes. In the soap-boiling process it is found to decrease materially the time required to cook a batch of soap.

ASPHALT REFINING.

Another use is found in asphalt refining where superheated steam in coils has taken the place of direct fires under the kettles. The danger of disastrous fires is avoided and the work is done in quick time. It is found that low pressure steam superheated will do as much work as saturated steam at a high pressure. Another process of a similar nature using superheated steam is that of pipe dipping. It is found that when the tank is maintained at a high temperature the coating applied to the pipe is not only smoother and more perfect, but also that less of the coating material is needed.

SUPERHEATING LOW-PRESSURE STEAM.

In connection with the superheating of low-pressure steam just mentioned, many manufacturers are finding the superheating of exhaust steam from their engines for process work a very desirable proposition. An interesting case of this kind is found in a large knitting mill where steam is first initially superheated for power uses, and after passing through the engines the exhaust steam is again superheated and used in pipe coils for drying purposes, and leaving these coils still slightly superheated travels 400 feet to a dye house where the latent heat is utilized for boiling dyes.

PAPER AND PULP MILLS.

Many advantages have been found in the use of superheated steam in the paper mill. General practice in such a plant now is to superheat the steam initially in the boilers using this steam in the engines, thereby saving 15 to 20 per cent. by the elimination of cylinder condensation and thus obtaining exhaust steam practically dry and free from moisture instead of containing from 10 to 15 per cent. of water. This dry steam although of less weight will do more work on the paper driers and it has been found that bleeding enough live superheated steam into this exhaust so that the steam on arriving at the ports of the paper drier contains 5 to 10° of superheat will give the highest efficiency. In some mills the available exhaust steam is insufficient to do the drying and in such cases the bleeding of sufficient live steam superheated into the exhaust not only gives the desired heat but by thoroughly drying and slightly superheating it makes it more efficient in the rolls.

A distinct advantage has been found in the use of superheated steam in digesters in pulp mills. Recent

tests in a large sulphite mill have shown that the time taken to reach the cooking point in the digesters was reduced from three hours, using saturated steam to two hours and to two hours and a quarter using steam superheated. Naturally this saving of time and reduction of water from condensed steam resulted in a less diluted acid solution at this point in the process and further saving in time during the rest of the process. This saving in time practically amounts to the same thing as a saving in fuel, or viewed from another standpoint the capacity of the digester for work is increased without an increase of fuel consumption. Another result also has been the possibility of obtaining the best of pulp from even very wet chips, which are sometimes difficult to use on account of dilution of the acid by this excess moisture.

COTTON OIL AND LARD REFINERIES.

Superheated steam is now very generally used in cotton oil and lard refineries for the purpose of deodorizing cotton seed oil. Also for similar work in linseed oil plants. This use for superheat has been especially successful.

WATER GAS PLANTS.

Still another interesting application is that in connection with water gas generators. Numerous installations of this character have been made and by blowing highly superheated steam through the incandescent bed of fuel it is possible to continue the blow for a longer period of time, due to the cooling effect of superheated steam being less than occurs with saturated steam and consequently a greater quantity of gas can be made per blow. In such cases superheated steam is also generally used throughout the whole plant, as the saving on the average engines and pumps used in such plants is large. The results are especially good in such cases, due to the fact that the pumps and exhausters do not run at the same time as the generators are in use and thus there is a practically continuous demand for steam.

EVAPORATION PROCESSES.

Superheated steam has found a distinct field where steam is used for evaporating purposes, especially in such plants where considerable power is also required and exhaust steam used for the evaporating work. Obtaining thoroughly dry exhaust steam for such purposes has been proved a decided advantage. A very successful application has been found in salt manufacturing plants where large quantities of exhaust steam are used for evaporation of brine.

SUGAR BEET PULP DRIERS.

Recent experiments in this country, following a practice already established in Germany have demonstrated the value of superheated steam in various forms of pulp driers in sugar beet refineries. In such plants where exhaust steam is used in the driers it has been found necessary to carry very high back pressures on the engines. By passing the steam after leaving these engines through a superheater it has been found possible to greatly reduce this back pressure and still obtain the same results in the driers.

thus making a large saving in steam, and increasing the power developed by the engines.

Numerous other cases of this character might be mentioned, but the above are typical and their chief interest lies in the fact that they represent such varied uses. New ways of utilizing superheated steam are continually being discovered and doubtless the above illustrations will serve to suggest new uses to the reader who is working along similar lines to those mentioned.

As noted earlier in this article, it is now possible to obtain superheater equipment designed to raise the temperature of the steam regardless of pressure to as high as 1100° to 1200° F. These superheaters if properly handled will give long service.

The various superheaters on the market may be divided into two classes: those installed within the settings of individual boilers and those in separate settings of their own, fired directly with any convenient fuel—either coal, oil, gas or wood. Superheaters installed within boiler settings can be designed to raise the temperature of the steam as high as 550 to 600° F. If higher temperatures than these are desired a direct fired superheater is necessary. Such direct fired units can, of course, also be used for lower temperatures and can be designed of just the proper size for any special use.

Where superheated steam is to be used for power purposes it might be stated that care should be taken to see that the apparatus used will furnish steam at a uniform temperature and especially in existing plants highly superheated steam is not to be recommended. As stated earlier in the article, American practice has proven that superheated steam at temperatures up to 500° F. can be used to advantage on almost any type of equipment provided a fairly uniform temperature is maintained, and it may be said that under these conditions practically no changes in design of piping, valves or fittings need be made over the usual construction in use for saturated steam conditions. In this way superheated steam can be utilized to advantage in a very large number of manufacturing plants, and large savings of steam and fuel obtained.

At the present time it might be said that the use of superheated steam in central power stations is more general than in manufacturing establishments, but a comparative study of its advantages in these two classes of plants shows that there is even more reason for its adoption in the latter than the former. The three factors on which percentage of return on an investment in superheater equipment depend, are first the cost of fuel, second the load factor or the hours per day run multiplied by the average percentage of the total equipment in service, and third the efficiency of the engine equipment.

In the average manufacturing plant access to the raw material is generally the primary object and the cost of fuel a secondary consideration. Thus in many such plants the cost of fuel is high and therefore a certain percentage saved will pay a high return on an investment to this end than would be possible where fuel is cheap.

In a large number of such manufacturing plants practically the whole boiler plant is operated and often twenty-four hours in the day, a far better condition than the central station can hope for, as they generally are called upon to furnish a heavy load for a small number of hours per day and have to, therefore, maintain a considerable portion of their equipment idle for a large part of the time, when the demand for power is light.

Lastly, the average manufacturing plant cannot afford to use as highly efficient equipment as the central station where the output of power is the chief object. It is practically true that the saving effected by superheating is about inversely proportional to the efficiency of an engine and the saving on engines of poor economy is relatively large as compared to one of very high efficiency.

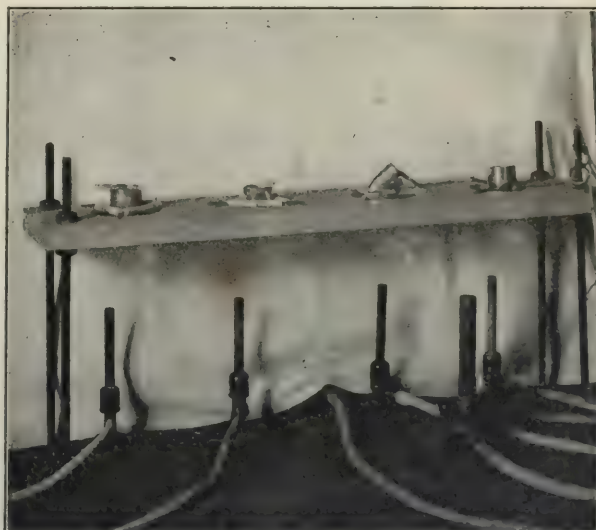
When in addition to these facts steam at high temperatures is desired for process work, it is easy to see why superheated steam is rapidly coming into use in the manufacturing plant.

A CONVENIENT CRUCIBLE SUPPORT.

By WILLIAM M. HORTON, JR., Chemist Virginia Geological Survey.

Received March 16, 1911.

The accompanying photograph shows a stand for supporting crucibles constructed of a rectangular slab of soapstone with circular holes, which is upheld by two iron legs at either end. The dimensions of the stone are $1 \times 6 \times 26$ inches. The holes are 3 inches in diameter, $2\frac{1}{2}$ inches from either end, and $\frac{1}{3}$ inches apart.¹ The legs are made of iron bolts $\frac{3}{8}$ inch in



diameter and $13\frac{1}{4}$ inches in length and threaded for $\frac{5}{8}$ inches, at the upper ends. The slab is held in position at the desired level by 2 nuts on each leg, one below and one above the stone. A Bunsen burner stands in readiness beneath each opening and can be

¹ The piece of stone cut as above described was supplied by the Alberene Stone Co., 223 E. 23rd St., New York, for \$0.50 f. o. b. quarry at Alberene, Albemarle Co., Va.

brought as close to the crucible as desired by blocks of wood of different thicknesses. The burner can be removed and replaced by the blast lamp and the crucible blasted if desired. The triangles employed have been for the most part the Hoskins chemists' triangles (made of a special nickel alloy) or those of vitreous quartz.

The apparatus has the following advantages:

(1) By using triangles of the materials just mentioned the crucible has perfectly clean surroundings, and the clean smooth soapstone furnishes an excellent surface on which to cool the crucible after a fusion or to rest the lid while examining the contents of the vessel.

(2) The apparatus is compact and is, hence, very convenient for ignitions or fusions while making the same determinations on different samples since they can be kept in order and similarly treated without the operator having to change his position.

The apparatus, as described above, has been in use by the writer in the laboratory of the Virginia Geological Survey for two years and has proven very convenient and entirely satisfactory.

GAS KILN FOR FIRING ORNAMENTAL GLASS.¹

The accompanying photograph shows the construction of a kiln for firing ornamental and stained glass, designed by the Laclede Gas Light Company, St. Louis. A track is extended on each end the full

interior surface of the walls exposed in the firing chamber is faced with the same material. There are two manifolds of fifteen burners each, one along each side of the kiln, the burners being placed through pipe castings in the walls so that the flames are projected horizontally on a plane about 1½ inches over the stock to be fired.

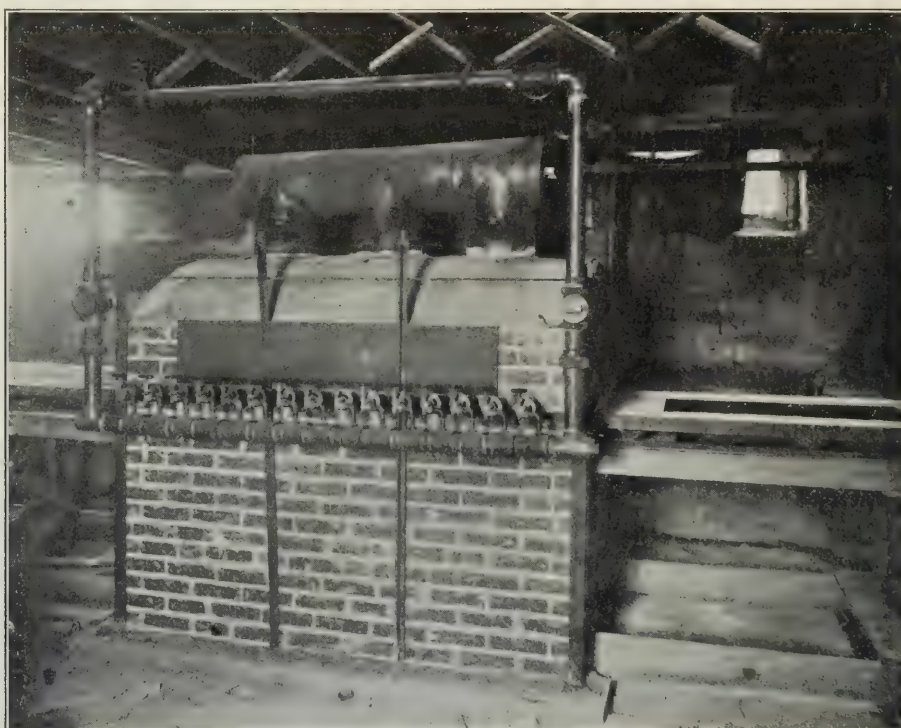
To avoid disturbing and cooling air currents, the end openings and those about the tray, also the vent above, are shut off to a point where perfect combustion and proper temperature are obtained. Atmospheric burners of about 50 cubic feet per hour capacity each, of needle valve type, are used, and from these the maximum consumption is from 1,200–1,500 cubic feet of gas per hour. The tray or carrier is especially constructed to insure against warping and bending due to the high temperature, 2,100° F. has been attained.

AUTOMATIC LIQUID SAMPLER.

By G. L. SPENCER.

Received March 27, 1911.

In THIS JOURNAL, 2, 253 (1910), I described an automatic device for sampling juice in cane sugar factories. Mr. August Wedderburn, superintendent of this company's "Tinguaro" factory, has slightly modified this sampler, thus making it applicable in withdrawing liquids from pipes under heavy pressure. The construction of the sampler is sufficiently de-



length of two trays to make possible the use of more than one tray for the purpose of continuous firing. The arched ceiling is constructed of fire brick, and the

scribed in the accompanying cut from a working drawing.

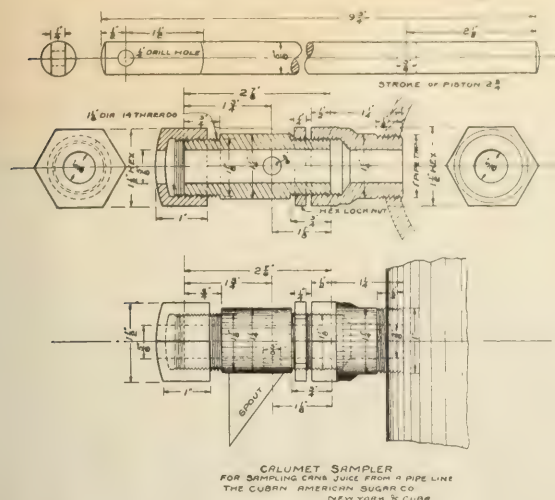
Obviously, the sampler should be operated by a mechanism that enables it to always draw the same

¹ Bulletin National Commercial Gas Association, April, 1911.

aliquot part of the material to be tested. In the case of a cane mill, this is readily accomplished by driving a crank shaft off a mill-roll shaft. In sampling

ing to the viscosity of the fluid. The dimensions given in the figure are those of samplers giving very excellent results with cane juices.

CUBAN-AMERICAN SUGAR CO.,
NEW YORK AND CUBA.



CALUMET SAMPLER
FOR SAMPLING CANE JUICE FROM A PIPE LINE
THE CUBAN-AMERICAN SUGAR CO.
NEW YORK & CUBA

sirop, connection may be made with some moving part of the pump conveying this material.

The size of the opening in the plunger should be varied to meet the quantity requirements and accord-

REFRACTORY CEMENTS.

During the past few years great progress has been made in the development of high temperatures produced by oil, gas, pulverized fuel, special design in furnaces, mechanical stokers, etc., which has caused considerable trouble in the maintenance of fire brick structures.

The Johns-Manville Co. have developed a material under the name J.-M. Brickline Cement which is especially adapted for coating over the exposed surface of fire bricks; it is claimed to be equally valuable on hard-burned or soft-burned bricks, inasmuch as the glaze that is formed by its application to the exposed surface of a fire brick structure reduces the porosity on the face of the brick and renders it impenetrable to the exceedingly destructive influence encountered. It increases the mechanical resistance of the brick, which better enables them to resist abrasion, etc.

SCIENTIFIC SOCIETIES

AMERICAN SOCIETY OF MECHANICAL ENGINEERS.

The local committee of the American Society of Mechanical Engineers, E. M. Herr, *Chairman*, Elmer K. Hiles, *Secretary*, having in charge the preparations for the Convention of the Society, which will be held in Pittsburgh, Pa., May 30th to June 2nd, inclusive, has nearly completed the work of arranging the program for each day during the meeting.

It has been settled that the arriving guests will be received and registered at the Hotel Schenley, the society headquarters, on Tuesday morning, May 30th. In the evening there will be an informal reception for the members and ladies in the parlors of the hotel. The extensive alterations being made by the new management of the hotel will add very largely to the comfort and enjoyment of visitors during the convention.

Professional sessions will be held in the Lecture Hall of the Carnegie Institute near the headquarters, Wednesday morning and evening, Thursday and Friday morning. In the meantime there will be a number of inspection trips to various industrial plants in the vicinity, a boat excursion for the members and ladies up the Monongahela River, a reception and ball at the Hotel Schenley on Thursday evening and, finally, on Friday evening a smoker and entertainment, given by the Engineers' Society of Western Pennsylvania, in their rooms, in the Oliver Building.

A carefully prepared program for the entertainment of the lady visitors has been arranged by a committee of ladies from Pittsburgh and vicinity, which includes a number of delightful social functions.

Judging from the number of inquiries, which have already been received from expected guests, a very large attendance is looked for, and everything indicates that this meeting in Pittsburgh will be one of the most successful "spring meetings" the society has ever held.

CONGRESS OF TECHNOLOGY.

A Congress of Technology presenting a record of the practical achievements of science in modern life was held in the buildings of the Massachusetts Institute of Technology in Boston, on April 10th and 11th. This occasion also marked the fiftieth anniversary of the granting of the Institute's charter, and the Congress is therefore in part a celebration of this anniversary.

A large number of addresses and scientific papers were presented representing a wide field of activity among the officers and graduates of the institute.

PROGRAM.

Address by the President.

Some Factors in the Institute's Success.

The Spirit of Alchemy in Modern Industry.—WILLIAM H. WALKER, Professor of Industrial Chemistry, Massachusetts Institute of Technology.

Technology and the Public Health.—C. E.-A. WINSLOW, '98, Associate Professor of Biology, College of the City of New York and Curator of Public Health, American Museum of Natural History, New York.

SECTION A.

Scientific Investigation and Control of Industrial Processes.

The Conservation of Our Metal Resources.—ALBERT E. GREENE, '07, Electro-Metallurgical Engr., Am. El. Smelting & Eng. Co., Chicago.

Some Causes of Failures in Metals.—HENRY FAY, Professor of Analytical Chemistry, Mass. Inst. Tech., Boston.

Metallography and Its Industrial Importance.—ALBERT SAUVEUR, '89, Professor of Metallurgy, Harvard University, Cambridge, Mass.

Thirty Years' Work in Boiler Testing.—GEORGE H. BARRUS, '74, Expert and Consulting Steam Engineer, Boston.

Coal Combustion Recorders.—A. H. GILL, '84, Professor of Technical Analysis, Mass. Inst. Tech., Boston.

An Electric Furnace for Zinc Smelting.—FRANCIS A. J. FITZGERALD, '95, Consulting Chemical Engineer, Niagara Falls, N. Y.

Improvements in Cotton Bleaching.—WALTER S. WILLIAMS, '95, Textile Expert, Arthur D. Little, Inc., Boston.

The Work of Engineers in the Gas Industry.—FREDERICK P. ROYCE, '90, V.-Pres., Stone & Webster Management Assoc., Boston.

The Chemist in the Service of the Railroad.—H. E. SMITH, '87, Chemist and Engineer of Tests, The Lake Shore & Michigan Southern Ry. Co., Collinwood, Ohio.

The Control of Thermal Operations and the Bureau of Standards.—GEORGE K. BURGESS, '96, Assoc. Physicist, Bureau of Standards, Washington, D. C.

The Debt of the Manufacturer to the Chemist.—HERVEY J. SKINNER, '99, Vice-President, Arthur D. Little, Inc., Boston.

Prevention and Control of Fires through Scientific Methods.—EDWARD V. FRENCH, '89, Vice-President and Engineer, Arkwright Mutual Fire Insurance Co., Boston.

Research as a Financial Asset.—WILLIS R. WHITNEY, '90, Director, Research Laboratory, General Electric Co., Schenectady, N. Y.

The Utilization of the Wastes of a Blast Furnace.—EDWARD M. HAGAR, '93, President, Universal Portland Cement Co., Chicago.

Development in Paint and Varnish Manufacture.—E. C. HOLTON, '88, General Chemist, The Sherwin-Williams Co., Cleveland, Ohio.

Reclamation of the Arid West.—FREDERICK H. NEWELL, '85, Director, U. S. Reclamation Service, Washington, D. C.

Some Problems of High Masonry Dams.—JOHN R. FREEMAN, '76, Consulting Engineer, Providence, R. I.

Some New Chemical Products of Commercial Importance.—SALMON W. WILDER, '91, President Merriam Chemical Co., Boston.

SECTION B.

Technological Education in Its Relations to Industrial Development.

The Engineering School Graduate; His Strength and

His Weakness.—H. P. TALBOT, '85, Professor of Inorganic and Analytical Chemistry, Mass. Inst. Tech., Boston.

Development of Mining Schools.—ROBERT H. RICHARDS, '68, Professor of Mining Engineering and Metallurgy, Mass. Inst. Tech., Boston.

The New Profession of Economic Engineering.—ROGER W. BABSON, '98, President, Babson's Statistical Organization, Wellesley Hills, Mass.

Instruction in Finance, Accounting and Business Administration in Schools of Technology.—HARVEY S. CHASE, '83, Certified Public Accountant, Boston.

Technical Education and the Contracting Engineer.—SUMNER B. ELY, '92, Vice-President, Chester B. Albree Iron Works Co., Allegheny, Pa.

The General Educational Value of the Study of Applied Science.—ALAN A. CLAFLIN, '94, President, Avery Chemical Co., Boston.

The Influence of the Institute upon the Development of Modern Education.—JAMES P. MUNROE, '82, President, National Society for the Promotion of Industrial Education, Boston.

The Training of Industrial Foremen.—CHARLES F. PARK, '92, Assoc. Professor of Mechanical Engineering, Mass. Inst. Tech.; Director of Lowell Institute School for Industrial Foremen, Boston.

The Responsibility of Manufacturers for the Training of Skilled Mechanics and Shop-foremen.—ARTHUR L. WILLISTON, '89, Principal, Wentworth Institute, Boston.

The Function of Technical School Laboratories.—H. W. HAYWARD, '96, Asst. Prof. App. Mech., Mass. Inst. Tech., Boston.

Technical Education—Its Function in Training for the Textile Industry.—CHARLES H. EAMES, '97, Principal, Lowell Textile School, Lowell, Mass.

The Contribution of the Institute of Technology toward Negro Scientific Thought.—ROBERT R. TAYLOR, '92, Director of Industrial Training, Tuskegee Institute, Tuskegee, Ala.

SECTION C.

Administration and Management.

An Object Lesson in Efficiency.—WILFRED LEWIS, '75, President, The Tabor Mfg. Co., Philadelphia, Pa.

The Scientific Thought as Applied to Railroad Problems.—BENJAMIN S. HINCKLEY, '99, Engineer of Tests, N. Y., N. H. & H. R. R. Co., Boston.

Reliability of Materials.—WALTER C. FISH, '87, Manager, Lynn Works, General Electric Co., Lynn, Mass.

A Consideration of Certain Limitations of Scientific Efficiency.—HENRY G. BRADLEE, '91, Stone & Webster, Boston.

Scientific Industrial Operation.—TRACY LYON, '85, Asst. to First Vice-President, Westinghouse Electric & Mfg. Co., Pittsburgh, Pa.

The Trend of Commercial Development Viewed from the Financial Standpoint.—CHARLES HAYDEN, '90, Banker, Boston.

Profitable Ethics.—DAVID VAN ALSTYNE, '86, Vice-President, Allis-Chalmers Co., Milwaukee, Wis.

The Natural Increase in the Ratio of Burden to Labor

in Modern Manufacturing Processes.—JAMES B. STANWOOD, '75, V.-P. and Engr., Houston, Stanwood & Gamble Co., Cincinnati.

Scientific Management of American Railways.—SAMUEL M. FELTON, '73, Pres., Chicago Great Western R. R., Chicago, Ill.

SECTION D.

Recent Industrial Development.

The Elimination of Some Sources of Loss in a Large Producer-Gas Engine Plant.—JOHN G. CALLAN, '96, Electrical Engineer, Arthur D. Little, Inc., Boston.

Improvements in Efficiency of Electric Lighting Properties and what the Public Gains Thereby.—WILLIAM H. BLOOD, JR., '98, Technical Expert, Stone & Webster, Boston, Mass.

Advent of Illuminating Engineering.—JOHN S. CODMAN, '93, Elec. and Ill. Engineer with the Holophane Co., Boston.

Development of Gasoline Engines.—JOSEPH C. RILEY, '98, Assistant Professor of Mechanical Engineering, Mass. Inst. Tech., Boston.

The Progress of Electric Propulsion in Great Britain.—HENRY M. HOBART, '89, Consulting Engineer, London, England.

Mechanical Handling of Materials.—RICHARD DEVENS, '88, Mgr. Eastern Office, Brown Hoisting Machinery Co., New York City.

The General Solution for Alternating Current Networks.—GEORGE A. CAMPBELL, '91, Research Engineer, American Telephone & Telegraph Co., New York City.

Electrochemistry and its Recent Industrial Development.—HARRY M. GOODWIN, '90, Professor of Physics and Electrochemistry, Mass. Inst. Tech., Boston.

Mail Handling Machinery at the Pennsylvania Railroad Terminal and United States Post Office at New York City.—JULIAN E. WOODWELL, '96, Consulting Engineer, New York.

The Development of a System of Underground Pneumatic Tubes for the Transportation of United States Mail.—B. C. BATCHELLER, '86, Chief Engineer, American Pneumatic Service Co., New York City.

The Continuous Cooling of Circulating Water Used for Condensing Steam.—EDWARD F. MILLER, Prof. Steam Engineering, Mass. Inst. Tech., Boston.

Power Plant Betterment.—H. H. HUNT, '89, Stone & Webster Management Association, Boston.

The Development of Economical Ore Dressing Systems.—FRANK E. SHEPARD, '87, Pres. Denver Eng. Works, Denver, Colo.

Recent Developments in Bridge Construction.—FRANK P. MCKIBBEN, Prof. of Civil Eng., Lehigh University, S. Bethlehem, Pa.

The Manufacture and Use of Asbestos Wood.—CHARLES L. NORTON, '93, Prof. of Heat Measurements, Mass. Inst. Tech., Boston.

The Technics of Iron and Steel.—THEODORE W. ROBINSON, '84, Vice-President, Illinois Steel Co., Chicago, Ill.

SECTION E.

Public Health and Sanitation.

Profitable and Fruitless Lines of Endeavor in Public Health Work.—EDWIN O. JORDAN, '88, Professor of

Bacteriology, University of Chicago, Chicago, Ill.

The Technical School Man in Public Health Work.—HARRY W. CLARK, '88, Chief Chemist, State Board Health, Boston.

Present Status of Water Purification in the United States and the Part that the Massachusetts Institute of Technology Has Played.—GEORGE C. WHIPPLE, '89, Consulting Engineer, New York City.

The Pollution of Streams by Manufacturing Wastes.—WILLIAM S. JOHNSON, '89, Sanitary and Hydraulic Engineer, Boston.

Sewage Disposal with Respect to Offensive Odors.—GEORGE W. FULLER, '90, Con. Hyd. Engineer and San. Expert, New York.

The Food Inspection Chemist and His Work.—HERMAN C. LYTHERG, '96, Analyst, State Board of Health, Boston.

The Life-Saving Corps of the Technical School.—SEVERANCE BURRAGE, '92, Prof. Sanitary Science, Purdue Univ., Lafayette, Ind.

Factory Sanitation and Efficiency.—C. E.-A. WINSLOW, '98, Assoc. Prof. of Biology, College of City of New York, New York City.

A Review of the Work of the Sanitary Research Laboratory and Sewage Experiment Station of the Massachusetts Institute of Technology.—EARLE B. PHELPS, '99, Consulting Sanitary Expert, New York City.

Bacteria and Decomposition.—SIMEON C. KEITH, JR., '93, Asst. Professor of Biology, Mass. Inst. Tech., Boston.

SECTION F.

Architecture.

Landscape Architecture, a Definition and a Brief Resume of Its Past and Present.—STEPHEN CHILD, '88, Landscape Architect and Consulting Engineer, Boston and Santa Barbara.

Some Phases of Modern Architectural Practice.—WALTER H. KILHAM, '89, Architect, Boston.

The Engineer and Architect Unite.—LUZERNE S. COWLES, '97, Assistant Designing Engineer, Boston Elevated Railway Co., Boston.

Mill Construction with Steel Frame and Tile Walls.—JOHN O. DEWOLF, '90, Mill Engineer, Boston.

INTERNATIONAL CONGRESS OF THE APPLICATIONS OF ELECTRICITY, TURIN.

An International Congress of the Applications of Electricity will be held at Turin, Italy, from September 9-20, 1911, under the auspices of the Italian Electrotechnical Association and the Italian Electrotechnical Committee.

The principal endeavor of the Organizing Committee, in drawing up the program of the Congress, has been to give the meetings a decidedly international character. The attainment of this object is aided by the fact that the first meeting of the International Electrotechnical Committee will be convened at Turin from September 11-16th, and the official delegates of the electrotechnical committees of several nations will be assembled there.

With the object of securing a definite and complete program of work at the Congress, the Organizing Committee has prepared an official list of subjects, for which it will appoint lecturers; but besides these it hopes that numerous papers will be presented by members of the Congress. The president of the Organizing Committee is L. Lombardi, and the secretaries are G. Semenza and C. A. Curti, 10 *via* San Paolo, Milan.

CONVENTION ON ENGINEERING EDUCATION.

The nineteenth annual meeting of the Society for the Promotion of Engineering Education will be held in Pittsburg, Pa., June 26th, 27th, and 28th. Headquarters for the convention will be at the Carnegie Technical Schools.

AMERICAN INSTITUTE OF MINING ENGINEERS.

At a joint meeting of the board of directors and of the council of the American Institute of Mining Engineers, on March 31st, Dr. R. W. Raymond tendered his resignation as secretary. His successor is Dr. Joseph Struthers, who has been assistant secretary during the last eight years. Doctor Raymond has been appointed Secretary Emeritus of the council, the institute thus retaining his services for special editorial and other duties for which he is so well qualified by training and experience.

INTERNATIONAL DAIRY CONGRESS.

It is announced that the Fifth International Dairy Congress organized by the Swedish Committee of the International Dairy Federation will be held this year at Stockholm from June 28th to July 1st. Former congresses have been held at Brussels, Paris, The Hague, and Budapest. At the close of the Congress an excursion will be made to Orebro, where the Twenty-first General Swedish Agricultural Convention will be held.

NATIONAL COMMERCIAL GAS ASSOCIATION.

The date of the Denver meeting has been changed to October.

At a meeting of the Board of Directors held in Chicago on Tuesday, March 15th, after careful consideration it was deemed advisable to change the date of the annual meeting as fixed by the association at its last convention, and a resolution was passed that the date of the Denver Convention should be the week beginning October 23, 1911.

WOOD TURPENTINE ASSOCIATION.

Specifications for Steam-distilled Wood Spirit of Turpentine
Adopted by the Wood Turpentine Association.

At the last regular meeting of the Wood Turpentine Association in Jacksonville, Florida, the association voted to adopt standards which the members of the association would adhere to in the manufacture of steam distilled wood spirit of turpentine and pine oil. These standards which were adopted as recommended

by the president, Dr. J. E. Teeple, are as follows for steam distilled wood spirit of turpentine.

First.—"Steam distilled wood spirit of turpentine shall be the pure, unadulterated and properly refined product, extracted from long leaf pine or fat light wood by steam or similar processes which act at a low enough temperature to avoid the conversion of the pinene into higher boiling compounds. This excludes destructive distillation products."

Second.—"The specific gravity should be as near as possible to 0.665 at 60° F., and should certainly lie within the limits 0.843-0.866."

Third.—"On distillation in the usual manner, it should not begin boiling below 305° F., and at least 88 per cent. of it should distil below 330° F. The undistilled portion at this temperature should consist only of higher boiling terpenes and terpene derivatives."

Fourth.—"Odor should be characteristic odor of wood turpentine, and the color to be water-white, and in other respects it should conform to the specifications applied by the Navy Department to gum spirit of turpentine."

A number of the plants are already making their turpentine in accordance with these standards and others have promised to follow as rapidly as possible, so that in the near future we may have this product standardized and marketed on the basis of Wood Turpentine Associations' Specifications, which will be a decided advantage to every one interested in these products.

For some little time there will no doubt be other products marketed which do not conform to these specifications, and the buyer can protect himself by inquiring in what respect the products offered fail to conform. For example, a product of destructive distillation can easily be identified by its odor, but if not, it will usually have a fairly low specific gravity and very much less than 85 per cent. of it will distil below 330° F., because the temperature reached in destructive distillation is sufficient to convert a considerable portion of the pinene into products boiling from 345-360° F.

A steam distilled wood turpentine which has been treated with acids or alkalies in the hope of improving its odor or removing objectionable products is also liable to have its point of distillation raised in the same manner, so that only 70 or 75 per cent. will distil below 330°.

Further, a pure steam distilled wood spirit of turpentine which has not been sufficiently refined whose specific gravity is as high as 0.868 or possibly 0.870, indicating that some of the pine oil by-product is still contained in it, will show a higher boiling point, only about 80 per cent. distilling below 330°.

If we assume, as is ordinarily done, that aside from the solvent properties pinene is a valuable product in turpentine, because of its ability to absorb oxygen, and that the higher boiling dipentene, terpinene, and terpinolene which have less oxygen-absorbing power are less valuable than the pinene, it would follow in a general way that the value of any turpentine would be measured by its percentage of pinene and similar

products, and so could be indirectly approximated by the amount which distills between 305° and 330° F. This is of course with the proviso that the product is absolutely free from any adulteration or addition.

INTERNATIONAL CONVENTION ON WEIGHTS AND MEASURES.

Dr. S. W. Stratton, Director of the Bureau of Standards, represents the United States government at the International Convention on Weights and Measures at Paris, beginning March 29th.

AMERICAN PHILOSOPHICAL SOCIETY.

The American Philosophical Society will hold its general meeting in the hall of the Society at Philadelphia on April 20th, 21st and 22nd. On the evening of April 21st, Professor Svante Arrhenius, of Stockholm, will give an illustrated lecture on the physical condition of the planet Mars, which will be followed by a reception in the hall of the College of Physicians. On the evening of the 23rd, the annual dinner of the Society will take place at the Bellevue-Stratford.

Dr. Svante Arrhenius, Director of the Nobel Institute of Stockholm, has been elected to honorary membership in the Chemists' Club of New York.

The Flavoring Extract Manufacturers' Association has appointed R. O. Brooks, formerly chemist for the New Jersey State Board of Health, as its official chemist.

About 130 fellows of the Royal Society subscribed for a portrait of Sir Wm. Crookes which was presented to the Royal Society on their behalf by Prof. Meldola.

NATIONAL ACADEMY OF SCIENCES.

The National Academy of Sciences held its annual meeting in Washington at the New National Museum, April 18-20th, at 2.15 P.M.

PROGRAM.

On the Motions of the Brighter Helium Stars.—W. W. CAMPBELL.

Report of Progress in Spectrographic Determinations of Stellar Motions.—W. W. CAMPBELL.

The Evolution of Periodic Solutions of the Problem of Three Bodies.—Lantern slides. F. R. MOULTON.

Mechanical Quadratures.—Lantern slides. G. F. BECKER.

Corollaries of the Theory of Isostasy.—W. M. DAVIS.
Experimental Investigation on Reflection of Light at Certain Metal-liquid Surfaces.—LYNDE P. WHEELER.

On the Origin of the Peaks of Maximum Pressure in the Midst of the Permanent Tropical Oceanic Highs.—W. J. HUMPHREYS.

A Further Study of Columbic and Tantallic Oxides.—E. F. SMITH.

The Outlook of Petrology.—J. P. IDDINGS.

The Orogenic Development of the Northern Sierra Nevada.—Lantern slides. WALDEMAR LINDGREN.

Biological Conclusions Drawn from the Evolution of the Titanotheres.—H. F. OSBORN.

A New Reptile from the Newark Beds.—W. B. SCOTT.

Restorations and Ontogeny of the Eurypterids.—Lantern slides. J. M. CLARKE.

A Geological Reconnaissance in the Rocky Mountains of British Columbia.—Lantern slides. CHAS. D. WACOTT.

Infantile Paralysis and Its Mode of Transmission.—SIMON FLEXNER.

Cell-size and Nuclear-size.—Lantern slides. E. G. CONKLIN.

The Cause of Death of the Unfertilized Egg and the Cause of the Life-saving Action of Fertilization.—JACQUES LOEB.

Studies of the Pulmonary Circulation.—HORATIO WOOD, JR.

An American Lepidostrobos.—Lantern slides. J. M. COULTER.

Aristotle's History of Animals.—THEO. GILL.

Notes on New England Mollusca.—E. S. MORSE.

Changes in Bodily Form of Descendants of Immigrants.—FRANZ BOAS.

Classification of Shoshonean Tribes.—Lantern slides. C. HART MERRIAM.

Biographical Memoir of W. H. C. Bartlett.—E. S. HOLDEN.

Biographical Memoir of C. B. Comstock.—H. L. ABBOTT.

Biographical Memoir of S. W. Johnson.—T. B. OSBORNE.

Biographical Memoir of Benjamin Silliman, 1816-1885.—A. W. WRIGHT.

Biographical Memoir of James H. Trumbull.—A. W. WRIGHT.

Biographical Memoir of C. A. White.—WM. H. DALL.

EDUCATIONAL

THE NEW LILLY SCIENCE BUILDING.

By June 1st, Eli Lilly & Company, of Indianapolis, will throw their new science building open to visitors and will welcome pharmacists and physicians to inspect it as it represents one of the best equipments of its class and is a fine illustration of the intimate connection of science and modern pharmaceutical manufacturing.

The outside walls are of red, hydraulic-pressed brick, with white terra cotta trimmings. The interior walls and floors are of re-enforced concrete, rendering the building fire-proof.

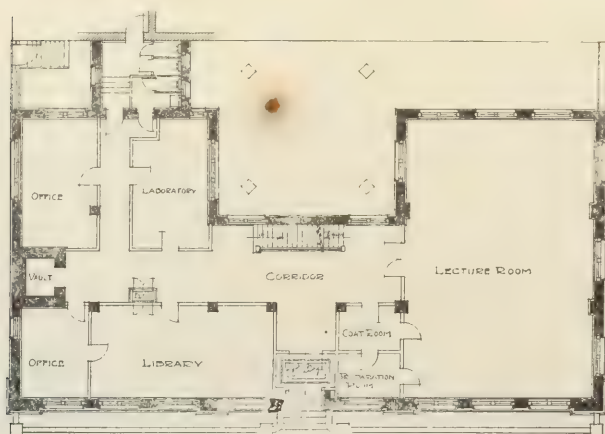
The basement will be used largely as a storeroom to supply the various departments with material for tests and experiments; a dumb waiter connects it with the other floors. In one corner is a shop equipped

with machinery and tools for repairing and manufacturing delicate apparatus employed in the scientific laboratories. The basement also houses a still for the preparation of distilled water for chemical and



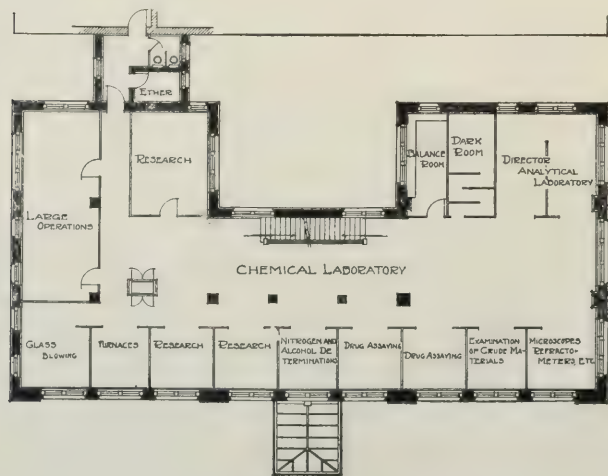
research work and a special milling equipment for grinding crude drug samples for chemical and physiological tests.

The first floor has a handsome street entrance pro-



First floor.

tected by a large glass canopy extending over the sidewalk. Across the north end of this floor is a lecture room capable of seating 200 comfortably. It is here that Lilly salesmen and department heads



Second floor.

will assemble to witness demonstrations and hear lectures upon subjects related to manufacture and sales work. The rostrum is provided with an experi-

ment table which is supplied with compressed air, water, steam, gas and electricity, ventilating hood, and exhaust. This lecture room is available to local scientific societies and for entertaining visiting classes from medical, pharmaceutical and other technical schools. Adjoining the assembly room is a small preparation room and storage for apparatus. One of the most interesting equipments of the lecture room is a modern projection apparatus adapted to regular lantern slides, microscope slides and opaque objects. Along the front of the building, south of the main entrance, as shown in the plan above, is a well-lighted, roomy library which will contain volumes of scientific and technical works with ample desks and other accommodations for the staff.

The second floor is occupied entirely by chemical laboratories for research and routine work. Some of the features of this floor are a dark room for spectroscopy, polariscope and other instruments of this class, a balance room with balances mounted on heavy stone shelves projecting from the masonry of the wall. Along the front of the second floor are nine alcoves, each a complete chemical laboratory in itself and large enough to accommodate two chemists. In one corner of the floor is a fire-proof room for ether and other inflammable liquids used in research work. There are also rooms specially designed for research, for large operations, and commodious quarters for the director of the analytical laboratory.

The third floor accommodates several departments; the botanical laboratory, with its large general herbarium of mounted plants and an immense collection of crude drugs in glass jars, is in the northwest section; connected with it by corridor and in the southwest corner of the floor is a conservatory of the latest type with workroom attached. This equipment enables the botanical department to conduct a number of experiments with plants throughout the year supplementary to the drug culture experiments which the department is carrying on in a larger way in the field near Indianapolis and in other parts of the country where climate is adapted to the species under investigation. On this floor there is also a bacteriological laboratory and a photographic operating room with a dark room. The remainder of the floor is occupied by the departments of pharmacology and experimental medicine.

CORNELL TO CONFER NEW DEGREE.

Hereafter the degree of Bachelor of Chemistry (B. Chem.) will be conferred by Cornell University on students who have completed the course in chemistry. The department of chemistry remains a department of the College of Arts and Sciences. A four-year course in chemistry and allied subjects has been offered by the department since 1903 for students planning to follow chemistry as a profession. Although the course is essentially technical in character and professional in purpose, the degree of Bachelor of Arts has heretofore been conferred upon its graduates.

TO ENLARGE COLLEGE SYSTEM.

The system of exchanging college professors between the United States and Germany will be extended so as to include technical instructors.

It is said that the first technical expert to represent the United States in this country will be Pherson Logan, who will lecture here on American Railways during the coming winter. Logan was a member of the commission which visited Germany in 1909 for the purpose of studying conditions in this country.

Ernest Meyer, an aero-technician, has been suggested as the German representative in America.

NEW UNIVERSITY BUILDING IN URUGUAY.

A remarkably handsome building, perhaps the finest of the kind in South America, has just been inaugurated for the Faculty of Law and Mathematics at Montevideo, Uruguay. It has been some four years building, at a cost of over \$2,190,000, and occupies a site of over 17,400 square yards, with imposing frontages to two main streets. As the accommodation provided is greatly in excess of present requirements, part of the building will be temporarily utilized to lodge the National Museum and Library until these have a building of their own, which is intended to be the case in a few years.

PRATT INSTITUTE, BROOKLYN, MAKES TERMS WITH NATIONAL TANNERS' ASSOCIATION.

In accordance with an agreement between the authorities of the Pratt Institute in Brooklyn and the National Tanners' Association, a school of training is to be established at the institute next fall.

This is to be the first school of the kind in the country. The institute will supply teaching facilities and equipment for 24 students, and the Tanners' Association will contribute \$5,000 a year for the next five years.

Mr. James R. Steers, of the class of 1853, has made a further donation of \$2,200 to the Wolcott Gibbs Library of Chemistry of the College of the City of New York.

Dr. E. B. Voorhees, professor of agriculture at Rutgers College and director of the N. J. Agricultural Experiment Station, has been granted a six months' leave of

absence, in order to enable him to recuperate from his recent illness.

Dr. H. T. Beans and Dr. Floyd J. Metzger have been advanced from instructor to assistant professors of chemistry at Columbia University.

Dr. Wm. McK. Marriott, assistant in physiological chemistry at Cornell Medical School, has been appointed instructor in biological chemistry in Washington University, St. Louis, Mo.

At the last meeting of the Rumford Committee of the American Academy of Arts and Sciences among other appropriations the following were made: To Prof. D. F. Comstock (Mass. Inst. Tech.) \$100 in aid of his researches on light. To Prof. G. N. Lewis (Mass. Inst. Tech.) \$150 to aid his work on chemical reactions. To Prof. R. W. Wood (Johns Hopkins Univ.) \$150 to aid him in his work on the optical properties of vapors.

At a meeting of the board of trustees of the Elizabeth Thompson Science Fund held in Boston a grant of \$150 was made to Prof. G. A. Hulett, of Princeton University, for further studies of the electrochemical equivalent and a grant of \$125 was voted to Prof. H. Freundlich, of Leipzig, Germany, for a research study on the kinetics of the transformation of aliphatic to aromatic compounds.

A bronze tablet in honor of Albert B. Prescott, formerly director of the department of chemistry at the University of Michigan, was recently dedicated at the opening of the new chemical building of the university.

The Missouri Legislature has made an appropriation of \$60,000 for a new laboratory of agricultural chemistry at the State University.

A prize of \$500 has been founded by the Mallinckrodt of St. Louis to be awarded to a chosen student of chemistry in the Graduate Schools of Harvard University for the year 1911-'12 on condition that the recipient will serve in the Mallinckrodt Chemical Works in 1912-'13 at a suitable salary.

OBITUARIES

BERNARD G. AMEND.

1821—THURSDAY, APRIL 6, 1911.

A modest, but nature-loving teacher in the city of Darmstadt, Professor Moldenhauer of the Realschule, now the Polytechnic, had a fancy to wander off afield with his pupils. He taught them simple truths in simple ways: interested them in minerals, in plant life, in chemical experiments, especially such as illustrated some natural phenomena. The seeds he

planted fell in fertile soil. Among his pupils were Liebig, Plattner, Hofmann, Merck and Amend. The latter, whose father was an officer in the civil service, chose pharmacy as a calling. As he grew he found his way to Giessen, where Liebig invited him to his lectures, and gave him the privilege of his laboratory which the young man eagerly took advantage of. Among the students was an American, E. N. Horsford, who urged young Amend to try his fortune in America, and held out some encouragement for an

assistantship at Harvard University, where Horsford became the Professor of Chemistry at the Rumford Scientific School. The young German followed the advice, reached New York, and as his means were scant, decided to settle down to work in that city. He took a small position in a drug store in Liberty Street, but soon left it to engage with Dr. William H. Milnor, who had a physician's office at the Northeast corner of Third Avenue and 18th Street. A pharmacy was connected with the office and over this young Amend presided.

While at the outskirts of the then city, this part of New York was, in 1848, close to the most fashionable neighborhood. St. George's Church on Stuyvesant Square, where Dr. Milnor's father had been pastor, was filled with a large congregation to listen to the eloquence of Stephen H. Tyng. Union Square was but a block away, while Gramercy Park was just to the north. Just beyond the latter the Free Academy, now the College of the City of New York, had been erected, and Wolcott Gibbs was Professor of Chemistry. The most noted families in the town had residences in this quarter and visited Amend at his store. Hamilton Fish, William M. Evarts, Samuel J. Tilden, Peter Cooper, Abram S. Hewitt, Cyrus Field, Washington Irving, Samuel B. Ruggles, Lewis B. Rutherford, Charles A. Dana, Bayard Taylor, Valentine Mott, James R. Wood, James W. Girard, and Howard Crosby were men of national, yes, of international importance. In 1851, Mr. Louis Gail and Mr. Amend purchased the business of Dr. Milnor, but the firm name which is best known is that of Eimer & Amend, Mr. Charles Eimer, a schoolmate of Mr. Amend having come over from Germany and entered the business in 1856. Although the firm name was thus framed, Mr. Amend and Mr. Eimer were equal partners in the business. For thirty-seven years the partners were associated without a written contract between them, a remarkable state of harmony, which had much to do with their continued success. From 1883-1897 the business was in Mr. Amend's hands solely, though the firm name was continued. It was then considered best to incorporate which was done under the laws of the State of New York. He was president of the corporation from its formation.

Though originally a wholesale drug house and pharmacy, it was deemed best later, when chemical laboratories began to spring up all over the country, to enlarge the business by adding a complete warehouse of chemical, physical, bacteriological and pathological outfits. Indeed as electrochemistry, metallography, and other special branches have appeared the necessary apparatus and special chemicals have been added to the ever-growing stock.

For many years Mr. Amend also indulged in his favorite study of minerals, and had a choice collection which he was most fond of exhibiting to his friends and intimate customers. The firm still has many of the finest of these.

Few pharmacists in the city took greater pride in their profession than Mr. Amend. Brought up under the severe school of Germany he brought with him

the highest ideals connected with the preparation and dispensing of drugs and medicines. His early association with the house of Merck enabled him to secure the newest preparations. As requirements advanced he met them, so that to-day the house is abreast of the critical demands of a numerous and exacting clientele.

Naturally he was interested in the College of Pharmacy. Professor R. Ogden Doremus was its Professor of chemistry from 1849-1860, and the lectures and laboratory exercises were held in the New York Medical College. When in 1871 the Board of Examiners in Pharmacy was appointed and all pharmacists had to secure certificates on passing a satisfactory examination, Mr. Amend complied with the statute and was examined by Professor Doremus, as President of the Board, and by the other members, and received his diploma. The functions of this first Board, are now in the hands of the Board of Pharmacy.

When the College of Pharmacy secured first its quarters in East 23rd Street, and later the fine building in West 68th Street Mr. Amend was liberal in his support of the institution of which he was a life member.

He was a member of the Lyceum of Natural History, which has since grown into the New York Academy of Sciences. Newberry, Joy, Van de Weyde, Torrey, Seeley, and later Bolton, were men who worked strenuously to uphold the dignity of their professions in that body, not to mention their survivors, who were also zealous. Mr. Amend was a member of the American Museum of Natural History, of the Museum of Art, and of the Chemists' Club, while his benefactions were dispensed, in part, through the agency of St. John's Guild and the German Hospital.

An original member of the first Board of Directors of the German Exchange Bank, he became later its first Vice-President, a position he retained to the end of his life. He is survived by two sons—Otto P. and Robert F.—who are in the business, and a daughter Mary L. Eimer, whose husband is a nephew of Charles Eimer, also an officer of the corporation.

Personally Mr. Amend was a modest man, but of untiring activity. His energies built up and directed the firm, and until within a few years he was actively engaged in conducting the business. Of a most kindly disposition, those with whom he came in contact always went away with pleasurable recollections of his courtesy and wide acquaintance with the very complex character of his pursuits. Few men retain their faculties to so great an age. His appearance changed but little as he advanced in years. Many will miss his kindly welcome, his genial smile. How wide and diverse the influence of those boys who went a Maying!

CHARLES C. DOREMUS.

MRS. ELLEN H. RICHARDS.

1842—MARCH 13, 1911.

The sudden death of Mrs. Ellen H. Richards at her home in Jamaica Plain, Mass., on the thirtieth of March, brought sadness to a large circle of co-workers and friends, and deprived sanitary science and home

economics of one of the most active and successful workers in these lines of public service.

Mrs. Richards was born in Dunstable, Mass., in 1842, the daughter of Peter and Fanny G. Swallow. In 1870 she was graduated from Vassar College, having devoted much time to astronomy as a pupil of Professor Maria Mitchell, and soon after she connected herself with the Massachusetts Institute of Technology where she was graduated from the course in chemistry in 1873. She married Professor Robert H. Richards in 1875. During the period from 1873-1884, Mrs. Richards gave a part of her time to teaching, but devoted most of it to the assistance of Professors John M. Ordway and William R. Nichols, the former maintaining an active practice in industrial chemistry, and the latter in sanitary chemistry. In both of these fields the work done was pioneer work, and especially that in sanitary lines demanded much originality of thought, skill in execution and breadth of outlook in interpretation. It was also during this period that the woman's laboratory was established in connection with the Institute to afford better opportunities for the education of women, and Mrs. Richards was the guiding spirit of that work, as she has since been of many of the other movements for the same cause. She later ('84-'94) became the chemist of the Manufacturers' Mutual Fire Insurance Co. In 1884 she became instructor in sanitary chemistry at the Institute, a position which she held at the time of her death, and has directed the instruction in the chemistry of air and water supplies at the Institute for the entire period, and that in food supplies for most of that time.

In 1887 the State Board of Health of Massachusetts began the survey of the inland waters of the state, upon a then unprecedented scale. The chemical examination was under the immediate direction of Professor Thomas M. Drown, but the success attending this immense undertaking, now a classic in its field, was in no small measure due to the coöperation of Mrs. Richards who brought to it a wealth of experience gained with Professor Nichols. She was chemist to the Board of Health from 1872-1875 and water analyst from 1887-1897, when the laboratories at the State House in Boston were established. She has constantly maintained an extensive private practice in the examination of waters for industrial, or household use and has published many papers and several books dealing with these topics. Some of her earlier papers and her constant interest in and association with the work of Professor Richards secured for her an election to membership in the American Institute of Mining Engineers, a distinction conferred upon only one other woman. She also maintained her membership in, and actively participated in the meetings of, various local and national societies dealing with water supplies and public health problems. As a teacher she was uniformly helpful and inspiring, and, with Professor Richards, she constantly extended the hospitalities of her home to her students.

Her contributions to sanitary science are so many and important that they would seem of themselves

to constitute a sufficient achievement for a busy life. But, great as these are, it is probable that she is still more entitled to lasting gratitude for her unflagging labors for the better education of women and the uplift of her fellow men. Preeminently a successful organizer and leader, she gave in recent years more and more time and attention to questions relating to the conservation of human life and energies, and her constant efforts to enable families of limited means to better utilize their moderate resources have borne much fruit. She became a recognized authority on matters of home economics and especially of dietaries and was the official adviser of many public and private institutions, and through her numerous writings and her lectures delivered in all parts of the country, she exerted a powerful influence for good.

It was a matter of great gratification to her many friends that Smith College conferred upon her the honorary degree of Doctor of Science in 1910. She has also been for many years a member of the Board of Trustees of Vassar College.

No brief statement can adequately express the fullness of Mrs. Richards' life or achievements. Always a tireless worker, without thought for herself, she literally wore herself out in the service of others, and spent the fading remnants of her strength in her last public speech in behalf of the cause which was so dear to her. Her work and high purposes will be perpetuated by the thousands whom she has inspired and taught, but they will miss her leadership, and unnumbered friends, the world over, will mourn her loss.

H. P. TALBOT.

HARRISON EVERETT ASHLEY.

1876—FEBRUARY 4, 1911.

By the death of Mr. Harrison Everett Ashley the American Chemical Society has suffered an irreparable loss on account of his unique contributions to the chemistry and physics of clay, and on account of his thorough and complete knowledge of the subject of inorganic colloids, with which he was better acquainted than any other chemist in this country and to which he was the most voluminous contributor to the literature in this country. While at the Massachusetts Institute of Technology, where he did his undergraduate work, he specialized in metallurgy and upon completing his course found employment in several steel plants and foundries. He was, however, while thus employed particularly interested in silicates, with especial reference to slags. As a result of this interest, he became acquainted with Professor Orton, and later took a practical position with a company engaged in the making of ceramic products. Later, realizing the necessity of more training in this line, he took a special course at the Ohio State University, where he was honored by an election to the society of Sigma Xi. After completing his graduate work, he was employed by the Homer Laughlin China Company at their large new plant in Newell, West Virginia. While there he began his study of the colloids in clays, doing so much work in this line that shortly after, when he became connected with the Technologic Branch of the

United States Geological Survey, he was able to issue one of his first papers upon this subject, "The Technical Control of Colloid Matters in Clays." He remained with the Geological Survey until his death, having been transferred with this branch to the Bureau of Standards in 1910. He had many opportunities, while thus engaged, to investigate and develop the new principles of colloids, as especially applied to clays, and worked very diligently in this line. He was the first to realize the close connection between the plasticity of clays and their colloid content, and by his many contributions to the literature of this subject and by his attendance at the various ceramic societies, he was able to bring this before the public and to interest many in his views. In this line he also contributed a paper on "The Chemical Control of Slimes."

Among his papers are the "Study of Tellurium

Alloys," "Slag Constitution by Means of the Tri-Axial Diagram," the "Pyro-Physical Behavior of Flint Fire-Clays," "Pottery Plaster," "Notes on Bolting Cloth Sizes," and a paper on the method of studying the "Gas Engine Cycle by Means of a Logarithmic Tri-Axial Diagram," published while he was at the Massachusetts Institute of Technology. Also a paper on "The Colloidal Matter in Clays," about to be published by the Bureau of Standards.

He was born at New Bedford, Mass., on August 2, 1876, of Puritan ancestry. He was educated in the public and high schools of New Bedford and the Massachusetts Institute of Technology, from which he was graduated in 1900 with the degree of B.S. in chemical engineering. He also spent two years at the Ohio State University in pursuit of his study of ceramics.

G. H. BROWN.

NOTES AND CORRESPONDENCE.

OUTPUT OF PLATINUM AND ALLIED METALS.¹

The conditions of platinum production in the United States, where the metal is obtained mainly as a by-product in placer gold mining, did not change materially during 1909, and the output of crude platinum in that year was 672 troy ounces of the reported value of \$12,803. The United States Mint obtains annually from its refinery operations a considerable quantity of platinum, the largest part of which is derived from scrap platinum and from sweepings, etc., bought from jewelers and dentists. A small percentage of primary metal is, however, obtained in refining gold bullion received at the mint. Because of the strong demand for platinum which has sprung up during recent years much secondary platinum is recovered in the United States from scraps of chemical apparatus, jewelry, dental work, and incandescent light fixtures.

The imports of platinum from other countries, chiefly Russia, were much larger in 1909 than in 1908 and 1907, but did not reach the values recorded in 1906. Platinum ore or crude platinum, including unmanufactured products, ingots, bars, sheets, and wire, was imported to the extent of 118,853 troy ounces in 1909, which had a value of \$2,557,596. Manufactured products, including vases, retorts, etc., worth \$416,352, were also purchased from foreign sources, making the total imports for the year \$2,973,948, in contrast with a total of \$1,229,873 during 1908. The average price for 1909 was \$24.98 per ounce. Owing to the scarcity of iridium the prices for "hard metal," which is an alloy of iridium and platinum, have gone up more rapidly than those for pure platinum. At the close of 1909 about \$35 per ounce was asked for hard metal. In addition to the many uses previously found for platinum, of late a strong demand for the metal has developed in the jeweler's trade.

FOREIGN PRODUCTION OF PLATINUM—IRIDIUM'S MANY USES.

The actual production of crude platinum in the

Urals in 1909 is estimated at 190,087 troy ounces. This output was smaller than usual, and it is probable that the reserves of workable areas are being exhausted. Almost all the platinum produced in Russia is refined in England, France, and Germany. During 1909 some progress was made in the platinum-bearing districts of Colombia, the exports of this metal to the United States in that year amounting to 2,392 ounces, in comparison with 1,092 ounces in 1908, according to the Bureau of Statistics. A little platinum was won in British Columbia; a production of 440 ounces was recorded from New South Wales; and Sumatra and Borneo are believed to have yielded about 500 ounces.

Iridium is generally present in crude platinum in alloy with osmium as iridosmine, more rarely as native metal or in alloy with platinum. In its manufacture from crude platinum it is obtained as a sponge, which is then melted with the addition of a little phosphorus. Its fusion point is 2150–2250° C. Under ordinary conditions iridium is not attacked by any acid. Most of the metal produced is probably used to harden platinum, the percentage of iridium in the alloys ranging from 5–20 per cent. Up to 10 per cent. the alloys are ductile and malleable; those containing 10–20 per cent. of iridium are hard and difficult to work; where the alloy contains 30 per cent. of iridium it is no longer attacked by aqua regia. Iridium is further used for scientific and technical purposes, such as standard weights, pivots, contact points, and fountain pen points. For certain high-temperature experiments iridium is rolled in sheets and welded into tubes. Pure iridium is difficult to work on account of its brittleness. Iridium black, an oxide of the metal, is highly valued as a pigment for decorating chinaware.

A few ounces of iridium are probably obtained from domestic crude platinum, but figures showing the quantity are not available. According to the Bureau of Statistics 341 pounds of iridium, valued at \$135,878, were imported in 1909 into the United States. The price of iridium has been increasing rapidly. In

¹ From advance chapters of Geological Survey publications.

1909 the average price was about \$35 per troy ounce, while in October, 1910, iridium was quoted at \$60 per ounce.

OSMIUM, PALLADIUM, AND RHODIUM.

Osmium generally occurs in combination with iridium. Its melting point is very high. Thus far little use has been found for it except for certain kinds of incandescent lamps. In 1909, according to the Bureau of Statistics, 4 pounds of osmium, valued at \$1,569, were imported into the United States.

Palladium occurs in crude platinum, but rarely in considerable amount. It is also found in small quantities in certain copper deposits containing pyrrhotite and chalcopyrite, generally associated with a little gold, silver, and platinum. It is malleable, has about the hardness of platinum, and a lower melting point than any other of the platinum metals. Palladium finds a fairly large use in technology. Circles of astronomical instruments are made of it, and it is also employed in watchmaking. Its most extensive use is probably for certain alloys in dental work. It is also employed for soldering platinum metals. The demand is considerably greater than the supply. In 1909 the imports of metallic palladium into the United States were 33 pounds, valued at \$13,416.

Rhodium is ductile and malleable at red heat; its melting point is about 2000° C. The metal occurs in crude platinum in amounts up to 4 per cent., and is also contained in platinum arsenide sperrylite. The principal use for this metal is for thermoelements employed in high-temperature determinations. The elements consist of pure platinum and platinum alloyed with 10 per cent. of rhodium. The price of pure rhodium is stated to be about \$155 per troy ounce.

ONTARIO MINERAL PRODUCTION.

The mineral production of Ontario in 1910 amounted to \$39,232,814, an increase of \$6,251,439 or 19 per cent. over 1909, according to *Bulletin 7*, of the Ontario Bureau of Mines.

Mineral production in 1910:

Gold.....	3,426 oz.
Silver.....	30,558,825 oz.
Cobalt.....	378 tons
Nickel.....	18,636 tons
Copper.....	9,630 tons
Iron (as pig).....	447,351 tons
Iron (as ore).....	88,169 tons
Zinc ore.....	576 tons
Arsenic.....	3,047,699 tons
Cement (Portland).....	2,471,837 bbls.
Corundum.....	2,692 tons
Feldspar.....	16,374 tons
Graphite.....	992 tons
Gypsum.....	10,043 tons
Iron pyrites.....	33,812 tons
Mica.....	513 tons
Petroleum.....	11,004,357 gals.
Quartz.....	90,685 tons
Salt.....	84,071 tons
Talc.....	7,112 tons

CUPROR.

Cupror, as described in *The Metal Industry*, is an alloy of copper and aluminum. Some really wonder-

ful results are claimed for it. Tensile strength of cupror in the bar is 93,000 pounds to the square inch. No. 20 gauge hard-drawn wire broke at 138,550 pounds to the square inch. The essential feature of cupror is its beautiful gold-like color and luster, these being really permanent and unchanging, even though subjected to conditions and usages of all kinds. The metal is also of extraordinary toughness and ductility, so that it can be drawn, spun and handled with the greatest facility. A complete description of cupror and its virtues is given in a small folder which has been issued by the Cupror Company, 50 Church Street, New York.

TIN MINED IN ALASKA.

The United States Geological Survey reports that in 1909 about 34,000 pounds of stream tin were mined in Alaska and shipped to England.

GAS PRODUCER EXPERIMENTS.

At the Experiment Station of the United States Bureau of Mines, Pittsburg, Pa., several trial runs have been made with an experimental gas producer, using coke as a fuel, with which limestone has been mixed in varying proportions, the purpose being to flux the ash and form a liquid slag, thus avoiding clinker and ash troubles and consequent shut-downs. Liquid slag has been readily made which runs freely from the producer. The high temperatures necessary are very efficient in the generation of gas.

GOVERNMENT POWER-SITE WITHDRAWALS.

Four new water power-site withdrawals, embracing 7,549 acres, were made during the month of March as a result of the field investigations of the United States Geological Survey. A total of 1,400,571 acres now stand withdrawn for power purposes, in the following states:

	Acres.
Arizona.....	107,550
California.....	53,689
Colorado.....	204,583
Idaho.....	231,698
Minnesota.....	3,619
Montana.....	126,047
Nevada.....	15,375
New Mexico.....	9,706
Oregon.....	161,777
Utah.....	347,252
Washington.....	80,386
Wyoming.....	58,889
Total.....	1,400,571

SULPHUR AND PYRITE INDUSTRY.

From a production of but 3,147 long tons of sulphur, valued at \$88,100, to an output of 239,312 long tons, valued at \$4,432,066, in a period of 10 years is a long stride, but this is the growth that has taken place in the sulphur industry in the United States since 1900. Furthermore, it was not so very long ago that the United States sent abroad more than \$3,000,000 annually for native sulphur, by far the larger part of which came from Sicily. In 1909 the United States

not only produced enough sulphur for her own needs but exported 37,142 long tons, valued at \$736,928, as compared with an importation of various grades valued at \$549,632, leaving a balance of trade in favor of this country of nearly \$200,000.

The great reversal of conditions whereby the United States has become a dominant factor in the sulphur industry of the world is largely due to the inventive genius of Herman Frasch, an American, of Cleveland, Ohio. The process whereby sulphur is obtained in practically pure condition from the earth is known from the inventor's name as the Frasch process and is employed in working the great sulphur deposits in Louisiana. Briefly the process is as follows: A well is driven in much the same manner as a gas or oil well is sunk, and into it are placed several concentric lines of pipe. Superheated water introduced through the outer pipe melts the sulphur, which may be several hundred feet below the surface. Hot compressed air is then forced through the smallest of the pipes. This forms an aerated emulsion with the molten sulphur, which is forced out by hydrostatic pressure between the remaining pipes and discharged in a purified form into large vats where cooling, solidification, and feeding go on simultaneously.

GOVERNMENT OIL LAND WITHDRAWN.

The petroleum lands in the public-land states constitute one of the most important natural resources remaining in the hands of the Federal Government. As a result of investigations by the United States Geological Survey large areas of these lands have been withdrawn from public entry pending legislation needed to prevent their wasteful exploitation. On April 1, 1911, these withdrawn oil lands aggregated nearly 4,000,000 acres. The states in which they are situated and the acreages are shown below.

	Acres.
Arizona.....	230,400
California.....	1,594,332
Colorado.....	87,474
Louisiana.....	414,720
New Mexico.....	419,901
Oregon.....	74,849
Utah.....	581,566
Wyoming.....	392,306
Total.....	3,795,548

MINERAL CHARTS.

The United States Geological Survey has issued its annual chart showing the principal mineral production in the United States in 1909. The aggregate value given is \$1,885,925,187. Owing to coöperation with the bureau of the census, which required unusually elaborate schedules, the issuance of this as well as of the numerous survey reports on mineral production for 1909 has been greatly delayed. Seventy different minerals are comprised in the list, and for comparison the figures of production are given for the past ten calendar years. In 1900 the total value of the mineral products of the United States was \$1,107,031,392, so that the increase during the decade was \$678,893,795.

Of the ten leading minerals in 1909, coal heads the list, with a value of \$554,902,624, which is more than the total mineral production in 1893 or 1894; iron is second with \$419,175,000; clay products third, \$166,321,213; copper fourth, \$142,083,711; petroleum fifth, \$128,248,783; gold sixth, \$99,673,400; stone seventh, \$71,345,199; natural gas eighth, \$63,206,941; cement ninth, \$52,797,973; and lead tenth, \$24,864,300.

CAMPHOR IN OIL OF SASSAFRAS.

In the *American Journal of Pharmacy*, 80, 220, Dr. Geo. R. Pancoast referring to the adulteration of oil of sassafras said: "One chemist has reported the finding of camphor in the oil, no doubt due to a small amount present in the camphor oil used for adulteration."

Without questioning the results of any chemist we decided it would be of interest to examine an oil known to be pure. Accordingly we prepared several hundred grams of oil by steam distillation of the roots of the sassafras tree. The oil had a slight yellowish color, possessed the specific gravity 1.0684 at 25° and showed a dextrorotation of 3.2° in a 100 mm. tube.

After removal of the phenol the oil was fractionated, first under diminished pressure and then at ordinary pressure. The fraction coming over at 204-210° was treated by the ordinary method for preparing oximes. There was obtained a substance of camphoraceous odor, which when recrystallized from diluted alcohol formed tabular crystals having the melting point 117°. The melting point of camphor oxime is variously given as 115-119°.

During the digestion on the water bath a white solid collected in small amount in the reflux condenser. This was another proof of the presence of camphor, as there is no known compound in oil of sassafras which could form such a sublimate.

THE IMPORTANCE OF COLLOID CHEMISTRY IN BREWING.

An excellent and interesting survey of the most recent work covering the subject of colloid chemistry was given by Mr. Jerome Alexander in an address to the New York Section of the American Society of Brewing Technology (meeting of January 25, 1911). After devoting a brief introduction to the history and earlier work in the field of colloid chemistry, supplemented by an explanation of the terminology, Mr. Alexander proceeds to show by way of concrete examples the applicability of the principles of colloid chemistry to a variety of industrial problems. There is practically no industry which is not involved either directly or indirectly, and the author's illustrations from agriculture, engineering, pottery, electrochemistry and soap manufacture are only a few among many others that could have been chosen. In the results of the author's own investigations on the application of colloid chemistry to milk, there are, perhaps, the best examples of the protective action of colloids. It is this same protective property of colloids which makes them such an important factor in the brewing

industry. In this connection the surface influences are of much importance. Thus for instance "by simply covering a mash with paraffin oil, Emslander found that the amount of albumen in the extract was reduced from 4.79-4.35 per cent." Similar changes are occasioned by contact with fluid or gaseous surfaces. The author suggests that the great influence of faces may be due in part to the traces of substances which they yield to the contained liquid. The question of the food value of beer was investigated by Emslander in a series of experiments suggested by the author's work on milk. The results showed a marked similarity. Colloids precipitated from beer had a powerful protective action on milk. It is this circumstance which imparts to the beer its tendency to render other foods more easily digestible. C. A. NOWAK.

GAS PRODUCER EXPERIMENTS.

At the Experiment Station of the United States Bureau of Mines, Pittsburg, Pa., several trial runs have been made with an experimental gas producer, using coke as fuel, with which limestone has been mixed in varying proportions, the purpose being to flux the ash and form a liquid slag, thus avoiding clinker and ash troubles and consequent shut-downs. Liquid slag has been readily made which runs freely from the producer. The high temperatures necessary are very efficient in the generation of gas.

GENERAL NOTES.

On March 24th the plant of the Vacuum Oil Co., in Olean, N. Y., was destroyed by fire involving a loss of \$200,000.

The Freeborn Construction Co., of Kansas City, has purchased 2100 acres of land near Pine Hill, Ky., as a site for a cement plant which will be designed to have a daily capacity of 1600 barrels of Portland cement.

The Vinton Oil & Sulfur Co., of Lake Charles, La., has recently been incorporated by A. Vincent, J. Lee Vincent and J. J. Dubourg with a capital stock of \$1,000,000 for the purpose of developing sulfur properties.

A sugar refinery is to be erected at Adeline, near New Orleans by Osnard & Sprague Co. to cost about \$500,000. It is to be the most complete and up-to-date refinery in the U. S. if not in the world. It will include a 12-roller mill.

The American Briquetting Co. has been organized at Dayton, O., with a capital stock of \$1,250,000 for the purpose of utilizing machines invented by A. D. Fernholz, of St. Louis, for pulverizing and compressing Texas lignite into fuel briquettes. It is claimed that lignite briquettes will burn without the formation of soot or smoke and that they can be sold at the mines for \$1.50 per ton.

The Corn Products Refining Co. recently announced that it had bought, about a year ago, control of the

Novelty Candy Co. with factories in Pittsburg, Jersey City, Memphis and Chicago. The cost was about \$500,000 and was paid out of the surplus. The capacity of the combined plants has already been doubled and it will be further increased until the total output rises to 300,000 lbs. per day.

E. B. Walden has been elected president of the Corn Products Refining Co. to succeed J. B. Reichmann. Mr. Reichmann is succeeded on the Corn Products board by William H. Nichols, Jr.

The U. S. Bureau of Standards has changed the value of the standard volt in this country to correspond with that used in England, France and Germany. The change although slight will be felt in the incandescent lamp industries, and is based on the value of the Weston cell at 20° C. Heretofore it has been customary to rate the cell at 1.091 volts, now the rating is 1.0183 volts. Hence our volt is made eight ten-thousandths (0.0008) larger than heretofore.

The Southern Electrochemical Company, of Charlotte, N. C., propose building a plant at Great Falls, S. C., for the fixation of nitrogen. The cost will be about \$125,000, and the annual output will amount to 2,000 tons on nitrate of lime.

American cement manufacturers shipped abroad last year 2,475,957 barrels, against 1,417,534 barrels in 1909, and 846,785 barrels in 1908.

The Buffalo Plant of the Wood Product Company was destroyed by fire on March 13th with a loss of \$250,000 fully covered by insurance.

Great Britain imported in 1909 from the United States 1,056,220 dollars worth of scientific instruments, and in 1910 3,804,400 dollars worth.

The production of natural gas in the United States in 1909, as ascertained by a joint canvass made by the United States Geological Survey and the Bureau of the Census, is estimated by B. Hill, in charge of this work under the supervision of D. T. Day, to have been \$55,000,000, an increase of only about \$359,626 over that of 1908. There were no great changes in the industry during the year, the production continuing to decline in Kansas, and an increase being made in Oklahoma and in the Caddo field in Louisiana and in Texas. An interesting feature was the supplying of Fort Worth and Dallas from the gas fields of Texas. For the year 1910 the total production is estimated at \$57,000,000, an increase of about \$2,000,000 over 1909. During 1910 a feature of great interest was the development of what promises to be a great supply of natural gas in the Buena Vista Hills, Kern County, Cal., east of the Sunset-McKittrick oil field. Arrangements were made and practically completed during the year for piping this gas to Bakersfield and other towns in San Joaquin Valley.

Creosote oil imports into the United States keep increasing. The amount last year was 42,608,386 gallons.

CONSULAR AND TRADE NOTES.

BEET-SUGAR PRODUCTION IN EUROPE.

Recent publications of the International Union for Statistics of the Sugar Industry estimate the production of sugar in the countries belonging to the Union at 7,540,000 tons in 1910-11, as compared with 5,780,000 tons in 1909-10, and in the non-union countries, Italy, Denmark, Spain, Switzerland, Roumania, Bulgaria and Servia, 408,200 tons, against 312,000 tons in 1909-10, a total European production of 7,948,200 tons, against 6,092,000 tons in 1909-10, an increase of 1,856,200 tons.

Germany retains its first place as a producer, with 2,500,000 tons; Russia comes second with 2,100,000 tons, while Austria-Hungary, which was second in 1909-10, takes third place in 1910-11. France with a decrease of 90,000 tons in 1910-11, occupies fourth place, and is the only country in the Union showing a decrease. Outside the Union, Italy and Denmark, with a production of 184,000 and 109,000 tons, respectively, are the only countries of any producing importance.

The percentage increase in the several countries in 1910-11, as compared with 1909-10, was as follows:

Germany, 23; Russia, 88; Austria-Hungary, 24; Sweden, 35; Holland, 10; France, a decrease of 11; in Belgium no change; Italy, 55; Denmark, 58; the other countries show no changes of any moment, with the exception of Spain, which shows a decrease of about 28 per cent.

To produce the foregoing amount of sugar in 1910-11 the 1,290 factories of Europe consumed 51,900,000 tons of sugar beets, as compared with 40,600,000 tons in 1909-10.

LEATHER TRADE OF RUSSIA.

Consul General John H. Snodgrass, Moscow, reports that the leather trade of Russia is worthy of close study and careful consideration by American manufacturers, evident from the following statement showing the imports of leather into Russia in 1909 and the first ten months of 1910, as classified in the customs schedules:

Description.	1909.	1910 (first 10 months).
Tanned, dressed with alum, tawed; chamois, calf, skins of fish and amphibious animals tawed thongs for sewing ends of machine belts.	\$3,754,865	\$4,489,770
Morocco, glacé, kid, shagreen, bearing stamped patterns, lacquered, etc.	2,046,095	1,839,580
Large skins: Ox, cow, buffalo, horse, ass, pig, in whole or half skins, without stamped patterns, grained or not, even with artificially stamped grain, dyed or undyed.	1,482,685	1,691,260
Parchment.	2,575	1,030
Lacquered skins, large.	1,254,025	1,367,325
Total.	8,540,245	9,388,965

The latest available statistics showing the imports of leather by countries are for 1908, but these hold relatively good for 1909 and 1910, and were as follows:

From Germany, \$6,188,120; Persia, \$330,326; France, \$259,991; United Kingdom, \$193,945; Austria-Hungary, \$193,662; United States, \$5,352; all other countries, \$833,318; total, \$8,004,714. This statement shows that the United States has a very insignificant place in this growing Russian trade.

GROWTH OF THE CLAY PRODUCTS INDUSTRY.

The statistics of mineral production for the ten years from 1900 to 1909, published by the United States Geological Survey, show a phenomenal growth in the clay products industry, the output for 1909 not only reaching the record mark of \$166,321,213, but showing an increase over that of 1900 of \$70,108,868 or 72 per cent.

SOAP FACTORIES IN ARGENTINA.

According to the general *résumé* of the industrial census of Argentina, recently issued by the office of commerce and industry of the Ministry of Agriculture, there are 200 soap factories in operation in Argentina, with a capital of \$1,096,070 United States currency, and selling annually \$3,014,304 worth of their products. One hundred and twenty-six of these factories are situated in the city and the Province of Buenos Ayres, while the remainder are distributed chiefly among the Provinces of the North. Nine hundred and forty-two persons are employed in this industry.

Notwithstanding the growth of this domestic industry, there are several brands of American soaps and shaving powders on the Argentine market.

Years.	Common. Kilos.	Perfumed. Kilos.	Medicinal. Kilos.
1908.	665,900	104,978	112,250
1909.	831,468	154,930	123,619
1910.	651,880	106,928	173,603

IMPORTS AND EXPORTS OF FERTILIZERS.

According to returns furnished by the Bureau of Statistics, the imports and exports of fertilizers into and from the United States during the years ended June 30, 1909 and 1910, were as follows:

IMPORTS.			
Kind and countries of origin.	1909.	1910.	
Guano:			
United Kingdom.	\$185,424	\$387,977	
Peru.	245,605	105,163	
Mexico.	45,146	45,717	
Netherlands.	75,672		
All other countries.	28,487	306,908	
Total.	580,334	845,765	
Crude phosphates.	137,006	152,840	
All other fertilizers:			
Germany.	3,684,490	4,603,238	
United Kingdom.	677,632	1,253,701	
Belgium.	228,287	466,738	
Canada.	362,854	436,173	
France.	97,702	273,334	
Netherlands.	113,245	78,598	
All other countries.	114,049	261,496	
Total.	5,278,259	7,373,378	
Total imports.	5,995,599	8,371,883	
EXPORTS.			
Kinds and countries of destination.	1909.	1910.	
Phosphate rock, ground or unground, not acidulated:			
Germany.	\$2,886,807	\$2,380,802	
United Kingdom.	944,240	1,074,772	
Netherlands.	930,886	950,845	
France.	978,608	621,584	
Italy.	682,371	580,520	
Austria-Hungary.	381,160	486,012	
Belgium.	457,512	446,862	
Sweden.	431,990	206,500	
All other countries.	412,210	706,797	
Total.	8,105,784	7,454,694	
All other fertilizers:			
Cuba.	512,445	559,808	
Canada.	450,734	489,792	
All other countries.	214,453	196,346	
Total.	1,177,633	1,245,946	
Total exports.	9,283,416	8,700,640	

The foregoing statistics do not include imports (1) of nitrate of soda from Chile, which amounted to \$16,601,328 in the cal-

endar year 1910, about one-third of which was used for fertilizer (2) of sulphate of ammonia, which amounted to \$4,668,820, chiefly from England, not (3) potash, which amounted to \$8,-363,632, mainly from Germany, and a very large portion of which was used as fertilizer.

GLYCERIN.

The total imports of glycerin into the United States during the year ended June 30, 1910, according to American official returns, amounted to \$3,665,763, viz.:

France.....	\$1,341,844
United Kingdom.....	1,143,873
Belgium.....	353,578
Netherlands.....	203,143
Italy.....	210,856
Germany.....	98,657
Spain.....	71,749
All other countries.....	242,063
Total.....	3,665,763

For the twelve months ended December 31, 1910, the American imports of glycerin were valued at \$3,799,553.

INCREASED LEAD PRODUCTION.

Despite a great gain in lead production due primarily to activity in the Southwest Missouri "disseminated lead" district, the production from domestic ores failed to reach the mark set in 1907; but this loss was more than made up by the increase in the production from foreign ores, so that the total production was the greatest ever recorded. Missouri and Utah both made good gains over their 1908 output, and each had the greatest production in its history. Missouri produced more than 40 per cent. of the total domestic output of the United States.

Features of the report are tables of general imports, imports for consumption, foreign exports, exports in manufactures, etc.

The following tabular statement issued by U. S. Geological Survey summarized the domestic and world's lead production:

	1907.	1908.	1909.
Production of refined lead in the United States.....	414,189	396,433	448,112
Production of desilverized lead in the United States.....	314,241	265,564	296,891
Production of soft lead in the United States (including desilverized soft).....	129,607	130,882	151,222
Production of antimonial lead in the United States.....	9,910	13,629	12,896
Total production of lead from domestic ores.....	365,166	310,762	354,188
Production of secondary lead in the United States.....	25,498	18,533	41,149
Consumption of lead in the United States (disregarding stocks).....	386,711	336,292	368,853
World production (approximate)	1,095,064	1,145,165	1,172,315
World consumption (approximate)	1,083,916	1,143,316	1,168,792
United States (domestic) percentage of world production.....	33.3	27.1	30.2
United States percentage of world consumption.....	35.7	29.4	31.5
World rank of United States in production of lead.....	First.	First.	First.
World rank of United States in consumption of lead.....	First.	First.	First.

THE PYRITE INDUSTRY.

Though the United States produced in 1909 nearly 250,000 long tons of pyrite, valued at more than \$1,000,000, this quantity did not meet the domestic requirements and the imports were nearly 700,000 long tons, valued at approximately \$2,500,000.

As large deposits of pyrite are known in Virginia, California, New York, and other States, it is to be hoped that these figures may be reversed in the not too distant future. Notes on the pyrite industry in the different States, together with tables of production, imports, and consumption, are given in a report on "Sulphur and Pyrite," by W. C. Phalen, just issued by the United States Geological Survey as an advance chapter of "Mineral Resources" for 1909.

REDUCED SALES OF ENGLISH COTTONS IN UNITED STATES.

The sales of British-made cotton cloth in the United States decreased last year. They amounted to 46,085,998 yards, worth \$6,607,795, against 61,451,676 yards, worth \$8,645,006 in 1909. These are statistics showing importations. Manchester exports to the Philippine Islands, however, increased last year by \$274,266.

SHUTTING DOWN INDIA TEXTILE MILLS.

Consul General William H. Michael, Calcutta, reports that mill coolies are leaving that city for their villages in large numbers for agricultural work, on account of the dearth of employment in the cotton mills there, of which 14 closed in January and six in February. This means that some 20,000 people will have been thrown out of employment. The closing is due to mills making no profit and heavy losses owing to the high price of cotton. Unless prices of cotton yarn improve proportionately to the enhanced price of cotton there is no hope of improvement.

The jute mills of Calcutta have agreed to work five days out of the week and to limit the hours from 5 A.M. to 8 P.M., instead of six days per week and sixteen hours per day. In the consequence of the new arrangement prices have advanced, and the mill owners will continue the arrangement, and if it shall seem necessary cut down the hours still more.

SOUTH AFRICAN TRADE NOTES.

Consul Edwin N. Gunsaulus, Johannesburg, reports that the value of the Rand gold industry to South Africa is estimated at \$500,000 a day.

The imports of machinery into South Africa for 1910 are estimated at \$17,500,000 as against less than \$10,000,000 in 1909. Mining and electrical machinery for the Rand constitute the greater portion of the imports.

The Union of South Africa now has, roughly, 7,000 miles of railway, which earns \$50,000,000 a year. Half of this sum paid out in working costs, the staff being 40,000, while nearly \$10,000,000 goes for interest. With a further deduction of \$8,325,000 for betterment and depreciation and other charges, there is a balance of about \$5,625,000 as a clear revenue to the government, by which the railways are owned and operated.

INVESTIGATIONS OF ARGENTINE OIL DEPOSIT.

The Department of State is informed by the American Minister of Buenos Ayres that a commission of civil engineers was appointed by the Argentine ministry of Agriculture to investigate the extent of certain oil deposits known to exist in the South-eastern part of Argentina, particularly in the district of Comodoro Rivadavia, Territory of Chubut.

This investigation is believed to be the outgrowth of a survey of this field made a year ago by an American capitalist, who is said to have offered to undertake its development by the expenditure of \$50,000 as an initial outlay. The Argentine government refused this offer and is now investigating the field directly.

BOOK REVIEWS.

Literatur der Zellstoff- und Papier-Chemie und der Papier-Technik im Jahre 1909. (Schriften des Vereins der Zellstoff- und Papier-Chemiker). By CARL C. SCHWALBE and ALFRED LUTZ. Verlag von Gebrüder Borntraeger, Berlin, 1911, 5 M.

The authors have undertaken in this book to abstract from forty-five journals the articles relating to the chemistry and technology of the cellulose fibers and paper.

Recent advances in the chemistry of the allied textile industries where cellulose is the basis, such as cotton, linen, jute, ramie, etc.; also the nitrocellulose explosives, celluloid and artificial silks have been abstracted.

The authors have divided the work into two parts:

Part I by Dr. Schwalbe, of Darmstadt, considers the chemistry of the cellulose and paper industries. This part contains 158 pages with an authors' and subject index. The subject matter is arranged as follows:

1. The chemistry and technology of the cellulose fibers.
2. Recent analytical developments.
3. Raw materials of the cellulose and paper industries.
4. Digestion of the cellulose fibers.
5. Bleaching.
6. Sizing.
7. Water used for manufacturing and power purposes.
8. Waste liquors.

Part II by Alfred Lutz, of Berlin, considers the manufacture and technical side of the cellulose and paper industries. This part contains 76 pages with an authors' and subject index and is arranged as follows:

1. Preparing of raw materials.
2. Digestion, washing, and bleaching.
3. Preparation of mechanical pulp, and pasteboard manufacture.
4. Shredding and screening.
5. Paper-making machines and paper manufacture.
6. Paper-finishing.
7. Special papers.
8. General.

The aim will be to continue this publication so that all interested will be able to obtain the abstracts instead of searching through the various scientific and technical journals. This will no doubt be of great interest to all connected with the cellulose industry.

OTTO KRESS.

Fibers used in Textile and Allied Industries. By C. A. MITCHELL and R. M. PRIDEAU. 1910. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. \$3.00 net, 190 pp., 66 illustrations.

In this book the author has attempted to bring together the latest microscopical and chemical-technical methods for the determining of the principal animal and vegetable fibers. The book deals with all the principal fibers used in spinning, weaving, cordage,

brush-making and upholstery, but does not include furriery or paper-making.

The arrangement of the subject matter is as follows: Introduction; wool; other animal fibers; silk; cotton; mercerized cotton; artificial silks; linen and ramie; jute and other cordage fibers; brush fibers; vegetable; downs and other upholstery fibers. Each of the fibers is considered briefly as to occurrence, preparation, uses, chemical composition, and as to methods for its chemical and microscopical identification.

The 66 illustrations, which, with three exceptions, were drawn specially by the authors, are well chosen, and representative, and are of great value for comparison in that they are, with few exceptions, drawn to the same scale. The authors not only have assembled the latest methods from the different scientific journals, but have added considerable from their own experience. References are given to the original article abstracted.

There are several typographical errors, the most serious one occurring on page 100, in which the oxygen content of the different nitrocelluloses as prepared by Vieille and adopted by Lunge should be 20 instead of 2.

The paper, printing, binding and general arrangement is good, and the authors have supplied a book which will be welcomed by all interested in the testing of textile fibers.

OTTO KRESS.

Essentials of Business Law. By FRANCIS M. BURDICK, D. Appleton and Company. 1910. xi+309 pp.

The name of the author of this little book speaks more forcibly for its merit and the care with which it has been prepared than any commendation which the reviewer can give. Its purpose, as stated in the preface, is to give the reader a knowledge of the essential principles of business law in clear and popular language, and this result has been accomplished to a remarkable degree. Indeed, it is believed that any lawyer who might read it would be surprised to learn with what simplicity and accuracy many legal principles can be stated and made intelligible to the non-professional reader.

The author disclaims any attempt to furnish a work which will enable the reader to be his own lawyer. It is in this respect that most of the authors of works on business law have erred. They have apparently endeavored, by furnishing a compilation of statutes of various states, to enable a man to act for himself in particular matters. These statutes are generally highly technical, not only in their phraseology but in their application, and no prudent man would attempt to conduct his affairs by the aid of such a work without legal advice. No book ever has been written and, in all probability, no book ever will be written which will make every man his own attorney.

Professor Burdick has approached his subject in an entirely different manner. He proceeds, in clear and simple language, to explain the important and funda-

mental principles underlying our system of law. Commencing with two interesting chapters on the origin of our law and the manner of its development, he then enters upon the specific subjects treated: Contracts, Agency, Bailments, Bankruptcy, Insurance, Negotiable Paper, Partnership, Joint-stock Companies, Corporations, Property and Sales of Personal Property. The care with which the work has been prepared is shown by the discrimination used, not only in the selection of subjects, but also in the treatment of only the fundamental principles involved and refraining from pursuing topics into their more technical fields, which would only serve to confuse the reader. The principles stated are frequently illustrated by concrete examples which greatly assist the reader to fully understand the application of the rule given, and throughout the text is readable and holds the attention.

No one, whatever his occupation may be, could read this book without profiting from it. He would not only be in a better position to appreciate his legal relations with those with whom he comes in daily contact in the course of his business dealings, but also would be able to discuss his affairs with his attorney with a more intelligent comprehension of the problems involved.

The author, in his preface, has intimated that the book is primarily intended for the instruction of young readers. Of its value in this respect there can be no doubt, but it is believed that the scope of its usefulness is much broader, and that even greater advantage can be obtained from it by persons of more mature years.

F. P. WHITAKER.

Chemistry of Food and Nutrition. By HENRY C. SHERMAN, PH.D.
viii+355 pp. The Macmillan Co. \$1.50 net.

The subject of food and nutrition may be approached by way of chemistry, by way of physiology, or by way of hygiene, pathology, or economics, and since students and investigators of the subject usually select one of these modes of approach, they are likely to see and present certain of its aspects more fully than others or to disregard some topics altogether.

In his "Chemistry of Food and Nutrition" Dr. Sherman is to be congratulated in that he has started with the subject of food itself. From this he moves outward to the consideration of the subject in all its important scientific bearings and connections. The result is a well-balanced treatise on food and nutrition, and not a volume on physiological chemistry, hygiene, or economics. However, such matters are discussed in their relation to the main theme.

The volume is primarily a text-book, the outcome of several years of teaching at Columbia University, and has been prepared for the use of the author's classes and other collegiate and technical students. It will however, also appeal to that growing number of general readers who consider that a knowledge of food materials is a necessary part of the equipment of a well-informed person, as well as to those who

think that such knowledge is essential to the maintenance of the highest body efficiency.

The general scope of the work is indicated by the following chapter headings: The Organic Foodstuffs, The General Composition of Foods and Action of Ferments, The Course of the Food through the Digestive Tract, The Fate of the Foodstuffs in Metabolism, The Fuel Value of Food and the Energy Requirement of the Body, Conditions Affecting the Total Food Requirement, Protein Metabolism and the Protein Requirement, Food Habits and Dietary Standards, Iron in Food and Its Functions in Nutrition, Inorganic Foodstuffs and the Mineral Metabolism, and Criteria of Nutritive Value and Economy of Foods.

The appendix contains tabular matter regarding the percentage composition, energy value, and ash constituents of the more common food materials.

The relatively large amount of space given in this volume to inorganic foodstuffs and mineral metabolism, a subject which Dr. Sherman has studied extensively is a matter for congratulation. When we consider how often the inorganic elements of food have received what may be called "lump treatment," and what a relatively small amount of trustworthy data are readily available on this subject, we are led to think that an extended treatment of this sub-topic tends to balance rather than to unbalance the general subject of foods. The tabular matter which shows the percentage amount of each mineral constituent in the edible portion, and also in a 100 calorie portion of the more common food materials will prove a great convenience, as will also the tables showing the percentage composition and energy value of 100 calorie portions of the more common foods.

The writer discusses fairly and at length two subjects, on which opinions have differed, namely, protein requirement and the absorption of inorganic iron by the animal body.

"Where a low protein diet is desired either for physiological or economical reasons," he suggests "an allowance of about 75 grams of protein per man per day, and for an average diet about 100 grams per man per day."

With reference to inorganic iron, he concludes that it probably does not enter into the hemoglobin molecule but that it acts as a stimulant to the production of hemoglobin and should therefore be taken not in place of, but in connection with, food materials rich in organic compounds of iron.

The entire discussion of this subject will be of great value to those who are interested in the problem of the proper feeding of children and young people.

While the size of the volume did not permit of extended discussion from an historical standpoint, the author has included such matter of this character as seemed most essential, and has provided references which will enable the student to readily find such additional material as may be required.

C. F. LANGWORTHY.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

WORKMEN'S INSURANCE.

Workmen's Insurance in Europe.—The remarkable progress made in recent years by foreign countries on the subject of employers' liability and workmen's compensation is brought out by the first two volumes comprising the Twenty-fourth Annual Report, just issued by the United States Bureau of Labor, Department of Commerce and Labor, entitled "Workmen's Insurance and Compensation Systems in Europe." This volume treats of Austria, Belgium, Denmark, France and Germany. Volume II, now in the hands of the printer, relates to Great Britain, Italy, Norway, Russia, Spain and Sweden. Although systems of insurance and compensation for cases of industrial accidents are the best known forms of workmen's insurance, the report shows that many European countries also possess a wide variety of insurance institutions for the relief of distress caused by sickness, invalidity, old age and unemployment. Besides these forms, the methods of providing maternity benefits for wage-earning women and the systems of pensions for widows and orphans of wage-earners are described.

TOPOGRAPHIC INDEX SHEETS.

The United States Geological Survey publishes, for the convenience of the public, index sheets which show the progress of the topographic work of the Survey in the several States. Any of these index sheets will be sent without charge on application to the Director of the Survey at Washington. The Survey's topographic maps have come to be recognized as of great importance to a large proportion of the people of any community, and those who use them will find the index sheet a great convenience in picking out the particular maps wanted. Most of the standard topographic maps are now published on the scale of about a mile to the inch and cover an area approximating 210 square miles. Over 2,000 maps of different scales have already been published, some surveys having been made in every State. Most of the maps are sold at 5 cents each.

WELL-DRILLING LORE.

The deepest well in the United States is near West Elizabeth, Pa. Its bottom is 5,575 feet beneath the surface. The deepest well in the world is in Germany and is 6,572 feet deep. A more remarkable well, perhaps, reaching a depth of 3,600 feet, was drilled for petroleum in western China by primitive methods and by means of such crude appliances as a cable made of twisted strands of rattan.

These facts and much other interesting information concerning underground supplies of water and oil and methods of getting at them are given in a report entitled "Well-Drilling Methods" by Isaiah Bowman, just published by the United States Geological Survey as Water-Supply Paper 257. The report is comprehensive and well illustrated, covering 130 pages and containing plates and figures, and may be considered one of the semi-popular publications of the Survey.

Proceedings of the National Commercial Gas Association; 6th Annual Meeting, December 5th to 9th, 1910, Mechanics' Building, Boston, with a description of the exhibition of gas appliances and a full catalog of the membership of the Association.

The following publications have been recently issued by the United States Geological Survey:

445. "Geology of the Pegmatites and Associated Rocks of

Maine, including Feldspar, Quartz, Mica, and Gem Deposits." By E. S. Bastin. 1911. 152 pp., 19 pls.

446. "Geology of the Berners Bay Region, Alaska." By Adolph Knopf. 1911. 58 pp., 2 pls.

447. "Mineral Resources of Johnstown, Pennsylvania, and Vicinity." By W. C. Phalen and Lawrence Martin. 1911. 142 pp., 7 pls.

470—A. Advance chapter from Bulletin 470. Contributions to Economic Geology (about papers and preliminary reports), 1910 Part I, "Metals and Non-metals except Fuels: Phosphates in Montana." By H. S. Gale. 1911. 9 pp.

Water-Supply Papers—257. "Well-drilling Methods." By Isaiah Bowman. 1911. 139 pp., 4 pls.

270. "Surface Water Supply of the United States, 1909, Part X, The Great Basin." Prepared by E. C. La Rue and F. F. Henshaw. 1911. 192 pp., 5 pls.

Mineral Resources—Separate chapters on antimony, arsenic, bismuth, and selenium; gold, silver, copper, lead, and zinc in the Eastern States; quicksilver; mica; anthracite coal; quartz and feldspar; slate; platinum and allied metals; fluor spar and cryolite; fuller's earth; sand-lime brick; gypsum; phosphate rock; abrasive materials; barytes and strontium; magnesite; borax; chromic iron ore; manganese ore; graphite; bauxite and aluminum; and iron ore, pig iron, and steel.

Bulletin of Canadian Department of Mines.—The Department recently published three pamphlets under the following titles: "Magnetic Concentration Experiments," "Preliminary Report on the Mineral Production of Canada," and "An Investigation on the Peat Bogs and Peat Industry of Canada." The latter goes into the subject of peat fuel to a considerable extent and contains a number of illustrations showing the methods of securing and drying the peat. Numerous maps and diagrams accompany this publication.

The Principles of Scientific Management. By FREDERICK WINSLOW TAYLOR, M.E., Sc.D. 8vo. Cloth. Harper & Bros. \$1.50 net. The author gives for the first time the full details of the system on which he has been working for thirty years.

Elements of Colloid Chemistry. (Part I.) By W. OSTWALD. Dresden. L. 8vo., 329 pp., \$2.50. 1911.

Inorganic Chemistry. (Part I.) By PERKIN and KIPPING. 12mo. 312 pp., \$1. J. B. Lippincott. 1911.

Practical Physiological Chemistry. By R. H. PLIMMER. 271 pp. \$1.80. 1911. Longmans, Green, & Co.

An Introduction to the Chemistry of Colloids. By VICTOR POSCHL. 12mo., 109 pp. \$1.25. 1911. J. B. Lippincott & Co.

Sewage Disposal Works. By HUGH P. RAIKES. 8vo., 429 pp. \$4. 1911. Spon & Chamberlain.

The Manufacture of Starch, Dextrose, Syrup and Caramel. By F. REHWALD. Vienna. 8vo., 272 pp. \$1.

An Introduction to the Study of Metallurgy. 6th Edition. By W. C. ROBERTS-AUSTEN. 8vo., 493 pp. \$6. 1911.

Electric Furnaces in the Iron Industry. By RODENHAUSER & SCHOENAWA. 8vo., 326 pp. \$4.50. 1911. O. Leiner: Leipzig.

Clarification of Sewage. By RUDOLF SCHMEITZNER. 8vo., 113 pp. \$1.50. Spon & Chamberlain. 1911.

Dynamic Biochemistry. By S. FRAENKEL. 1911. Wiesbaden. L. 8vo., 601 pp. \$1.50.

Capillary Chemistry. By HERBERT FREUNDLICH. 1911. Akademische Verlagsgesellschaft, Leipzig. 8vo., 591 pp. \$4.75.

RECENT INVENTIONS.

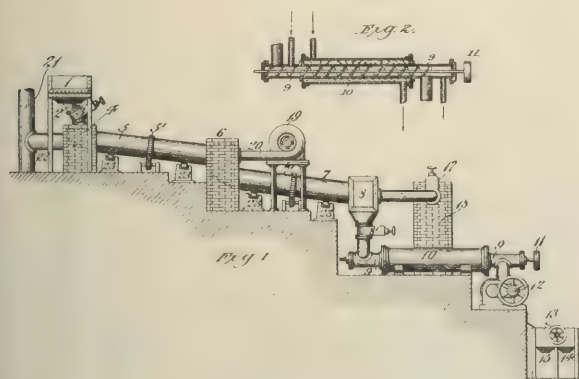
Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

986,086. Reduction Plant for Treatment of Metallic Sands or Concentrates.

This invention is an apparatus for the reduction of iron sands or concentrated ore, which is received at the plant in a finely pulverized condition.

The object of the invention is to produce a furnace or reduction plant which can be operated with gas such as is generated from the distillation of wood, or in the manufacture of coal into coke or peat or kindred substances.

In the apparatus illustrated, 1 designates a bin of suitable size and construction to receive ore as it is delivered from the mines and from which the chute 2 conveys the same by means of a valve, 3, to a chamber, 4. From this chamber 4 the ore is delivered to a furnace, 5, here shown in the preferred form as a rotary furnace, operated in any suitable manner, as by the gear 5'. This is preferably composed of a steel shell provided with a suitable lining, as brick, and is positioned to discharge into an air-tight chamber, 6, from which the ore is led to another rotating furnace, 7, of similar construction to that before described, and operated in a like manner by gear 7'. The function of the furnace 5 is to first heat the ore to a suitable temperature ready for delivery to the furnace 7, the exit end of which is located



adjacent to a chamber, 8, of air-tight construction and from which the discharge of ore is controlled by means of a valve, 8'. The opening of this valve 8' allows the ore within the chamber 8 to pass to a conveyer, 9, preferably of spiral type, operated by a revolving shaft driven by a pulley, 11. This spiral conveyer 9 is operated through a water-jacketed chamber, 10, in order to cool the ore as it passes through the conveyer.

12 designates crushing rollers suitably positioned adjacent to the discharge end of the conveyer 9 and upon which the ore is deposited as it is delivered at regular intervals. These rollers crush the ore to a suitable fineness ready for separation, which preferably takes place by passing the ore over magnetic separators, 13, from which it is delivered in the respective bins 14 and 15. These bins at the completion of the separation contain the two products produced, iron ore and dross. It will of course be understood that if the ore contains non-magnetic particles of value, that other means of separation may be used, such taking the form of wet or dry concentration, as the case may be.

The gas used in preparing the ore is generated in a retort furnace, 18, and is preferably made from the distillation of wood or coal. This gas is conducted at a high temperature under pressure through the conduit 16 into the chamber 8 and thus through the reduction furnaces to the furnace 5 in which it combines with a sufficient amount of air to maintain combustion and pre-

heat the ore. The air necessary to support combustion in the furnace 5 is furnished by means of a blower, 19, from which it is delivered by a pipe, 20, to the furnace 5, and after passing there-through is exhausted through the pipes 21 and 22.

The inventor is George Frederick Rendall, of New York, N. Y.

New Dyestuffs Derived from Indigo and the Production Thereof.

British Patent 17818/09.

Max Wyler & Levinstein, Ltd., Manchester.

Claims (1) the process of producing new dyestuffs which consists in treating in the presence of sulphuric acid indigo white or indoxyl or indigo with nitrosophenol or its homologues and then treating any of the new compounds thus obtained with bromine in the presence of nitrobenzol and subsequently heating the thus obtained mixture, all substantially as hereinbefore described.

Manufacture of New Vat Dyestuffs of the Anthracene Series and Intermediate Products.

British Patent 133/10.

Society of Chemical Industry in Basle.

Claims (1) the manufacture of anthranols by treating para-chlorobenzylbenzoic acid, para-methylbenzylbenzoic acid or chloromethylbenzylbenzoic acids (derived from ortho-chlorotoluene and para-chloro-toluene) with a suitable condensing agent; (2) the manufacture of benzanthrone derivatives by treating the anthranols obtained according to Claim 1 with glycerine or a substitute therefor and a condensing agent; (3) the manufacture of benzanthrone derivatives by treating the derivatives of benzylbenzoic acid mentioned in Claim 1 with a condensing agent in presence of glycerine or a substitute therefor; (4) the manufacture of new vat dyestuffs by heating with a caustic alkali the benzanthrone derivatives obtained according to Claims 2 and 3; (5) as new products the anthranols, benzanthrone derivatives and dyestuffs manufactured as above set forth.

Process for the Production of Colored Wool Effects in Half Woolen Goods Dyed in the Piece.

French Patent 416,906.

Farbwerke vorm Meister Lucius & Brüning in Hoechst.

Claims half woolen consisting of undyed wool and cotton is mixed with woolen threads, dyed in any shade, but protected against the action of dyestuffs by having been treated with astringents and metal salts. If the pieces are then dyed the cotton and wool are dyed the same or different shades, but the woolen threads remain unchanged. Thus the pieces finally show two different shades of wool and different colored cotton.

Improvements Relating to the Artificial Production of India Rubber or Caoutchouc.

British Patent 15299/09.

R. W. Wallace and G. A. Morton, London.

Claims (1) the treatment of material consisting of or containing certain substances of the terpene series, which natural rubber or latex-containing micro-organisms, or cultures of the bacilli or enzymes obtained therefrom, substantially as and for the purpose specified; (2) the treatment of isoprene or its homologues or material containing the same, consisting in subjecting the isoprene or the like to the action of anaerobic bacilli obtained from natural rubber or latex, or from other sources, or enzymes obtained with such bacilli, substantially as described and for the purpose specified; (3) artificial rubber and the method of producing the same substantially as described.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF APRIL.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Acetanilid.....Lb.	20 1/2 @	23
Acetone (drums).....Lb.	13 @	15
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	2.25 @	2.40
Acetic Acid (28 per cent.).....C.	1.62 @	1.74 3/8
Acetate of Lime (gray).....C.	1.75 @	1.80
Acetate of Lead (brown, broken).....Lb.	7 3/4 @	8
Aniline Oil.....Lb.	11 1/2 @	11 3/4
Benzoic Acid.....Oz.	11 1/4 @	12
Boric Acid, crystals.....Lb.	7 @	7 1/2
Carbon Tetrachloride (in drums).....Lb.	8 1/8 @	12
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (in drums).....Lb.	10 1/2 @	11 3/4
Citric Acid (domestic).....Lb.	38 1/2 @	39
Camphor (refined in bulk).....Lb.	— @	49 1/2
Dextrine (imported potato).....Lb.	5 1/2 @	7
Dextrine (domestic corn).....C.	2.12 @	2.28
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....Lb.	22 3/8 @	23
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7.20 @	7.75
Pyrogallie Acid (bulk).....Lb.	1.00 @	1.05
Paraffine (crude) 120 @ 122 m. p.....Lb.	3 @	3 1/4
Paraffine (refined), domestic 120 @ 122 m. p.....Lb.	4 1/2 @	4 3/4
Salicylic Acid.....Lb.	31 @	33 1/4
Starch (corn).....C.	1.37 @	1.53
Starch (potato).....Lb.	4 @	5 1/4
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 7/8 @	5 1/4
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	29 1/4 @	29 1/2

Inorganic Chemicals.

Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (in drums) 16°.....Lb.	2 3/4 @	3
Ammonium Chloride, gray.....Lb.	6 1/8 @	6 1/4
Arsenic, white.....Lb.	1.96 1/4 @	2.06 1/4
Ammonium Carbonate, domestic.....Lb.	8 @	8 3/4
Aluminum Sulphate.....Lb.	90 @	1 3/4
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 3/4
Barium Nitrate.....Lb.	5 1/2 @	6 1/2
Borax, crystals in bags.....Lb.	3 1/2 @	4
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.20 @	1.30
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	— @	4 1/4
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	93 3/4 @	95 3/4
Chalk (light precipitated).....Lb.	4 1/2 @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (in bags).....C.	62 1/2 @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 1/8 @	8 3/4
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	84 3/4 @	87 3/4
Nitric Acid, 36°.....Lb.	3 7/8 @	4 1/4
Nitric Acid, 42°.....Lb.	4 7/8 @	5 1/4

Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25
Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 3/4 @	11
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals, f. o. b. works.....Lb.	8 1/4 @	9 1/2
Potassium Nitrate (crude).....Lb.	4 3/4 @	5
Potassium Bichromate, 50°.....Lb.	7 3/8 @	7 3/4
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	75 @	77
Salt Cake (glass-makers).....C.	62 1/2 @	77 1/2
Silver Nitrate.....Oz.	34 @	36
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 1/2 @	5
Sodium Chlorate.....Lb.	8 1/4 @	9 1/2
Sodium Bicarbonate (English).....Lb.	2 3/4 @	3
Sodium Bichromate.....Lb.	5 5/8 @	5 3/4
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 1/2
Sodium Hydroxide, 60 per cent., f. o. b. works.....C.	1.80 @	1.85
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.	6 3/4 @	10
Sodium Nitrate, 95 per cent., spot.....C.	— @	2.10
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 3/4 @	10
Strontium Nitrate.....Lb.	7 3/8 @	7 3/4
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	90 @	1.00
Talc (American).....Ton	15.00 @	25.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	12 1/2 @	12 1/2
Tin Oxide.....Lb.	45 @	47
Tin Chloride (36°).....Lb.	11 @	11 1/2
Zinc Chloride (granulated).....Lb.	4 1/2 @	4 3/4
Zinc Sulphate.....Lb.	2 1/4 @	2 1/2
Zinc Dust.....Lb.	6 3/4 @	7

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 1/4
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	10 @	20
Corn Oil.....C.	6.44 3/4 @	6.48 3/4
Cottonseed Oil (crude), f. o. b. mill.....Gal.	40 @	40 3/8
Cylinder Oil (light, filtered).....Gal.	19 1/2 @	20
Japan Wax.....Lb.	9 1/4 @	9 1/4
Lard Oil (prime winter).....Gal.	95 @	1.05
Linseed Oil (raw, city).....Gal.	92 1/2 @	93 1/2
Linseed Oil (double-boiled).....Gal.	95 @	96 1/2
Paraffine Oil (high viscosity).....Gal.	23 1/2 @	24
Rosin Oil.....Gal.	— @	36
Spindle Oil, No. 1.....Gal.	14 @	14 1/8
Stearic Acid (double-pressed).....Lb.	10 @	10 1/2
Sperm Oil (bleached winter) 38°.....Gal.	82 @	85
Tallow (acidless).....Gal.	63 1/2 @	70
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum [No. 1 ingots].....Lb.	20 2/3 @	21 1/8
Antimony.....Lb.	8 1/2 @	9
Bismuth.....Lb.	1.80 @	1.90
Copper (electrolytic).....Lb.	— @	12 1/8
Copper (lake).....Lb.	12 1/8 @	12 1/8
Lead.....Lb.	4.41 7/8 @	4.43 3/4
Mercury.....Lb.	61.3 @	61.5
Nickel.....Lb.	40 @	45
Platinum (refined).....Oz.	41 @	41.50
Silver.....Oz.	— @	56
Tin.....Lb.	37 3/4 @	43 3/4
Zinc.....Lb.	5.4 @	5.45 3/4

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EDITORIALS

A SURVEY OF CYANIDATION IN 1911.

The advances made in the last ten years in the art of cyaniding ores of gold and silver have taken place so rapidly that few men are aware of the extent to which the field of application of the process has widened. Indeed, these changes and improvements have followed so fast on the heels of one another that even the men engaged in the practice of cyanidation are at times ignorant of the later developments. The change has been gradual, and one of the most striking things about it is the chemistry of the process which is little advanced today over what it was ten years ago. Essentially a hydrochemical process, all the improvements have been mechanical and though we may have a better knowledge of its chemistry, that knowledge is of little use to us in solving the problems connected with it. The essential advantage of cyanidation over other hydro-metallurgical processes is its chemical simplicity. Various workable processes have been devised that improve on the present cyanide process in theory, but in practice, the fact that they require a higher degree of metallurgical skill for their successful application, will always prove a bar to their adoption if cyanidation will do the work almost as well. There undoubtedly will be ores of gold and silver that cyanidation will not extract the values from and we can turn to other processes when that is so. The great variety of ores treated by cyanidation makes one feel that where a gold or silver ore is concerned, in at least nine cases out of ten, cyanidation will make a better extraction at a lower cost than any other process.

Cyanidation was first practiced on the sand or granular portion of the tailing, from mills treating quartzose, gold-bearing ores. It was not regarded as suited to silver ores at first but soon was found to be applicable to them, though it made only a 60 per cent. recovery, because it did so at such a low cost.

These first plants were percolation plants and could only operate when part, or all, of the slime, or colloidal portion of the ore, was run to waste. The decantation plants of South Africa were an effort to solve the problem of treating slime that never fully succeeded. The most marked advance in cyanidation began when the submerged suction filter was brought to such a state of mechanical efficiency that it was generally applicable. The two best known exponents of this principle in this country are the Moore and Butters filters, though I believe the idea was previously employed by Cassel in South Africa in a less efficient form.

The submerged suction filters not only made it possible to treat all the slime but even made it desirable to reduce as much of the ore as possible to nearly a slime condition. These new conditions created new demands and a host of clever mechanical appliances has been perfected to meet them. It was no longer possible to bring the finely ground ore in contact with cyanide solution by passing the solution through the ore, as in a percolation plant, so this was achieved by mixing the ore and solution together and keeping the ore suspended in the solution by means of agitation. Unconsciously the tremendous improvement in extraction possible through finer grinding has been learned until now cyanidation presupposes fine grinding, agitation and filtration.

At present, gold and silver ores varying widely in chemical composition, and in value from \$4 to \$35 in gold, and from a few ounces to thirty ounces in silver, are being successfully cyanided. Cyanidation has displaced pan-amalgamation. The cost of cyaniding is lower, the extraction better and pan-amalgamation only was suited to ores essentially of silver, whereas cyanidation extracts both gold and silver. Lixiviation, with the necessity of previous roasting, costs much more to practice, makes a poorer extraction

of silver and none of the gold. Chlorination likewise requires roasting of the ore and makes no extraction of the silver. Even where an ore is so rebellious that it must first be roasted, cyaniding has displaced chlorination and lately the ores of Cripple Creek and Cobalt, chemically complex and hitherto considered hard metallurgical problems, are now successfully treated in the raw state, when low grade, by cyanidation. The last field to be invaded, and one in which the possibilities have not been reached, is that of concentrate treatment. Hitherto the concentrate produced by gold and silver mills was always shipped to the smelters, in many cases an uneconomical proceeding—but now every few months adds another to the list of concentrates that can be successfully cyanided. Simple ore-dressing—that is, amalgamation and concentration—will hold its own for some time to come on the low-grade ores to which it is suited, because the preparation of the ores is less elaborate and the whole operation can be performed for about one-third of the cost of cyanidation. Even then, the concentrate will probably be treated by cyanidation and wherever the grade of the ore is high enough to justify the expense of making a higher extraction, cyanidation will be preferred.

Most of these processes require a high order of metallurgical skill, but cyanidation can be successfully practiced by men of no technical education and little knowledge of chemistry.

The development of the process has consisted purely in refinement. Cyanide mills are now elaborate structures in which there is a special device employed for every possible operation. This high efficiency has been attained at the cost of flexibility, and smooth continuous operation is essential to low cost. The tendency in mill practice is to relieve the operator of the necessity of exercising his judgment and to place more responsibility in the hands of the designer. The function of the mill-man now is to understand his machinery and keep it in operation, but the extraction that the mill makes depends on that machinery being properly adjusted in the design of mill.

The cost of mills has increased enormously. This has made it advisable to employ a better standard of materials in their construction and more care in their design. A degree of thoroughness is exercised in testing previous to design that was unheard of a few years ago. Then standard mill construction involved 850 lb. stamps, wooden mortar blocks and framing, and three tons per stamp per day was regarded as good practice; the rough approximation generally accepted for mill construction was \$1,000 per stamp. This was equivalent to a cost for construction of \$335 per ton of daily capacity. Later the increased cost of materials and labor and the increase to 1050 lb. in the weight of stamps, with the consequent daily capacity of five tons per stamp, made \$2,000 per stamp the figure, equivalent to \$400 per ton of daily capacity. Now, the advent of the fine-grinding, agitation and filtration plant has so added to the machinery installed in mills, that the role of the stamp has been altered so that it can no

longer be taken as a basis for estimation and \$1,000 per ton of daily capacity will often be found as the correct figure for mill construction. The variation in cost is greater, however, and an estimate must be gone into with more care than formerly was the case. The standards of construction have changed. A wooden mortar block now excites more comment than a concrete one did seven years ago. Steel framing, concrete floors, retaining walls and foundation all are common practice.

The mills all resemble one another so that they virtually conform to a type. Those that differ from the type remain different not because they are better but because it would cost too much to change them. Every modern cyanide plant now involves fine-grinding, settling of the pulp to greater density and removal of the surplus solution, agitation, further settling and filtration. Crushing, in the majority of cases, is performed wet. The reason for the wide-spread adoption of this process to the exclusion of all others and of this type of mill is found in the cost and the extraction. The cost of cyanidation seldom gets below 50 cents per ton, but it should never exceed \$1.50 per ton. The extraction of gold should always be from 90 to 95 per cent., and of silver from 88 to 92 per cent. These results, which are so frequently attained in practice that they can be expected, make cyanidation an art, with the wide-spread application of which every metallurgist should be familiar.

ARTHUR R. TOWNSEND.

THE GENERAL MEETING IN JUNE.

Those chemists who were fortunate enough to listen to the remarks of Charles F. Chandler during the banquet at the opening of the Chemists' Club last March will not soon forget the earnestness of his description of the growth of the coöperative idea among American chemists. Having been among the very first in this country to organize a small group of men interested in chemistry and having been one of the small number who met around Priestley's grave in Northumberland, Penn., August 1, 1874, which meeting resulted in the organization of the American Chemical Society, he spoke with authority. The chief tenor of his advice was to "get together," and those who know him well know that he as well as others of the pioneers in American chemical science have exerted their full influence throughout their lives to induce American chemists to get together for their own advancement and the advancement of the profession. The point cannot be too strongly emphasized for its practical embodiment is seen in the remarkable growth of the American Chemical Society in the last twenty years and the wonderful influence it has had upon the development of chemical industry in America and upon the increase of individual knowledge and endeavor among American chemists.

The Local Sections of the Society afford means of personal contact with chemists in limited localities and these Local Sections have done a great and good

work in developing the spirit of helpfulness and fellowship among their members. Altogether too few of the members of the Society, however, attend the general meetings which occur semi-annually. It is true that attendance at these meetings is rapidly increasing, but it has not yet reached the point that can reasonably be expected, and it is hoped that the members of the Society will carefully consider this point and make every endeavor to be present at Indianapolis and future gatherings of the general Society.

No member who has not been a regular attendant at the general meetings can realize the wonderful help they may be in the development of the individual. They give opportunity of meeting chemists in all kinds of work, thereby broadening the knowledge of the individual; they give opportunity of meeting chemists who are interested in the same lines of work and thereby frequently add to the specific facts which are important in special industries; they give opportunity of meeting the most successful chemists both in industrial and educational work and thereby add inspiration—they give opportunity for visiting special industrial works, adding to the practical knowledge of the visitor; they give opportunity for a summer or winter outing, for every Local Section does much to entertain its guests.

Many chemists feel that they cannot afford the time and expense of attending these meetings. Most of those who do attend, especially after they have been two or three times so that they become acquainted, realize that they cannot afford to stay away even if the distance is great and time is pressing. Especially the young or isolated chemist who has not the opportunity of frequent intercourse with his fellows, who is too apt to get into one line of thought, cannot afford to stay away, for the friendships made and the inspiration gained through knowledge of the work of others will make him a better chemist and is certain in the end to add to his material as well as to his mental advancement.

It is particularly pleasant to see the changing attitude of many of our most prominent firms towards attendance at the general meetings of the Society. A few years ago chemists complained that they found it difficult even to get the necessary leave of absence to attend the meeting. Now the case is quite often reversed. Firms have found that they gain so much by the presence of their chemists at these meetings that those who have had experience have almost invariably not only allowed the necessary time for attendance but in many instances now insist upon attendance and in an increasing number of cases pay all the expenses of the chosen individual. These cases are as yet altogether too few, but they are yearly increasing and it is indicative of a broader and more successful American chemical industry. It is certainly true that it is the most progressive and successful firms that require their chemists as a part of their work to attend the general meetings of the American Chemical Society.

Special efforts are being made to have the summer meeting in Indianapolis a great success, and definite

assurance can now be given that every member who attends the meeting will have unusual opportunity both for enjoyment and for professional development. The Entertainment Committee is planning an interesting program for the entertainment of ladies, and it is certain that they, too, will find the meeting unusually attractive. An especially amusing program is promised for the smoker on one evening; the following evening an automobile ride to the Country Club with lunch on the grounds, lawn fete, dancing, music, etc., is expected; on the third evening the usual banquet will be held. Two full days will probably be given up to the meetings of the Divisions, while the morning of the first day will be given to general addresses of interest to all chemists. One afternoon those present are to be especially entertained at the dedication of the new laboratories of the Eli Lilly Company, one of the largest pharmaceutical manufacturing companies in America. Saturday will probably be given up for the main part to visits to manufacturing plants.

Begin to plan now for the summer meeting. Remember the date is Wednesday, June 28th, to Saturday, July 1st; the place, Indianapolis. Let us all "get together" there!

CHARLES L. PARSONS.

ENDOWMENT FUND.

No organization which does a great and broad public service should be without the resource of available funds to promote and further the work.

On every hand we see a continual and worthy effort being made to stabilize and make sure of a continuous performance such endeavor.

Why the American Chemical Society should not take advantage of the very apparent opportunity is hardly understandable. Here awaiting us for action are to be found the ideal conditions under which a most successful effort can be undertaken. An organization composed of a body of men representing all classes, working for a great common good, namely, the advancement of chemical knowledge, with the best field for its application.

With an intangible valuable attribute to the goods to be delivered—working brains; a market for these same goods, which is boundless; an unsatisfied demand for the best obtainable execution measured by the ability of the individual and the effectiveness made possible by the organization as a unit, what more could be asked or could be offered which would appeal to the users and consumers of such a product, namely, the body corporate, The American Chemical Society? We who are of it should individually and all together determine upon a course which will enable the Industrials of this country to benefit by an open-minded, free-for-all research in all branches of chemistry, giving to the struggling young chemist inspiration by opportunity, and to the manufacturers at large an appreciation of unrestricted research, the benefit of which can be enjoyed by all to the great advancement of the industries of this country.

That an endowment fund would properly take care of this need is very apparent, and in one way only

can such a fund be made available—absolute and complete cooperation with a well defined plan of action carefully thought out and made the interest of every director, councilman, division chairman, sectional chairman and member.

In order to secure the opinion of the Society as a whole we take this opportunity to place an insert in this issue, and request your prompt reply to the questions of the Chairman of the Endowment Committee.

B. T. B. HYDE.

ORIGINAL PAPERS.

THE MICROSCOPIC EXAMINATION AND IDENTIFICATION OF CARBON.

By G. A. ROUSH.

Received March 28, 1911.

The remarkable success which has in the last few years attended the application of microscopic methods to the examination of the structure and properties of metals and alloys suggested an attempt to apply the principles of metallography in the examination of carbon. The carbons of commerce are made up of small particles of one or more of the different varieties of amorphous carbon cemented together by means of a binder, usually tar or pitch. The object of this investigation was, if possible, to develop some distinguishable difference in the appearance under the microscope of these ultimate particles of carbon, by which they could always be recognized, in order that the composition of unknown materials might thus be determined.

The wide-spread uses to which carbon is being put nowadays, and the variety of raw materials which may enter into the composition of carbons of different classes and grades has made desirable a method for the differentiation of various raw materials which may have been used, and an approximate analysis of the composition of any particular sample. The principal commercial uses of carbon are for arc light electrodes of various kinds, electrodes in furnace and electrolytic processes, electrodes for dry and wet batteries, brushes for dynamos and motors, contacts and resistance material in electrical apparatus and machinery.

Such a wide scope of uses as are shown here necessarily implies a considerable number of available raw materials which may be used to give the carbons the distinctive properties best suited for their particular uses. The list of available materials includes the following:

Lampblack		
Retort Carbon		
Petroleum Coke		
Graphite	Natural	Powdered
	Artificial	Flake
Coal Coke	Bituminous	Bee Hive
		By product
	Anthracite	Gas

Coal coke is at present used very little, if any, on account of its high ash content, but it is a possible available material for future use, provided some process can be devised to remove the ash, or for some use where the presence of the ash is not detrimental. Lampblack is used most in the high-grade arc carbons, and to a small extent in some grades of motor and dynamo brushes. Electrodes are mainly of petroleum coke, sometimes of retort

carbon and sometimes of a mixture of these two. Motor and dynamo brushes may be composed wholly of retort carbon, petroleum coke or one of the varieties of graphite, or of mixtures of two or more of these materials, with occasionally a small percentage of lampblack, as stated above.

Heretofore there has been no means of even approximately estimating the composition of products of this kind, except by judging from appearance, and comparing with trial mixtures. Hence the determination of the composition, or the duplication, of a sample of unknown composition was a matter of considerable difficulty, which, it is hoped, will be somewhat lessened by the results of this investigation. The results here described are not as full and complete as might be desired, but those obtained are given as a step in the right direction, with the hope of adding to them in the future.

Methods.—The methods are simply those used in the examination of a sample of a metal or alloy to determine its internal structure. These can be found in full in any standard work on metallography, and so will be given only briefly here. The method in general consists in selecting a suitable sample of the material in question, grinding on one side a flat surface by means of an emery wheel, and then bringing this flat surface to a smooth polish by rubbing it successively on emery papers of increasing fineness. After a perfectly smooth polished surface is obtained, the structure of the material is developed by etching the surface by means of some suitable etching medium, and the prepared surface is then ready for examination under the microscope, the object being, as stated before, to develop some distinguishable difference in the appearance of the particles of which the material is composed, by which they can be recognized and distinguished.

Preparation of the Samples.—The samples should be selected so as to be as representative as possible, and several different sections should be prepared so that the results obtained may represent a fair average of the material in question. In order to accomplish this, the samples examined should include sections, the polished surfaces of which were originally perpendicular to each of the three principal axes of the original sample, since the orientation of the particles of carbon varies with the shape of the particle and with the shape of the die through which they are forced.¹ The samples to be examined are best removed from the entire mass by means of a hack saw. The surface to be prepared is first flattened by touching to an emery wheel or dressing with medium rough file. The further polish-

¹ Those not familiar with the manufacture of carbon are referred to the writer's article on this subject in *THIS JOURNAL*, May, 1909.

ing of the sample then consists in removing the scratches left on the surface by one grinding medium with a succeeding one of finer grit. The emery or file can be followed by rubbing on an emery paper of No. 1 or No. 0 grade, and this is followed by successive grades of Crocus paper from No. 0 to No. 0000. The sample should be rubbed on each paper so that the scratches produced are at right angles to those produced by the preceding paper, since by this means it can be most easily determined when all the scratches of the preceding paper have been eliminated. A few rubs over the surface of the No. 0000 Crocus paper usually suffices to fill the grit of the paper with finely divided carbon from the sample in hand so that the surface is given a more or less mirror-like polish, which is the result desired. The steps necessary to obtain such a polish vary widely with the different materials. In some cases only two or three of the different polishing papers are required, and with others one may have difficulty in obtaining the desired results at all. Some samples give satisfactory results at first trial, while others require repeated attempts before they finally give a surface that can be examined with any satisfaction. It is a matter that can be learned only by experience, since every individual piece requires its own individual treatment.

After the specimen is polished, it has to be given a further treatment in order that the structure may be distinguished. The surface must be treated in such a manner that the softer parts of the material are worn away more than the harder, so that in this manner the structure of the material is left in outline. This may be accomplished in one of two ways: the sample may be heated to a red heat so that the air attacks and oxidizes the polished surface, leaving the denser and more resistant parts in outline, or the surface may be still further polished on a soft, yielding material such as chamois skin or broadcloth, so that the softer parts are worn away more rapidly than the hard, thus leaving the outlines in relief. In the further descriptions the former is known as "heat etching" and the latter as "relief polish." These two different ways of finishing the specimen give a somewhat different final appearance, and the question as to which is the more suitable for a given sample can be decided only by trial. It is often of benefit to prepare samples in both ways and compare them with each other. No set rule can be given as to the amount of etching necessary, as this varies with the different samples, but usually, if heat-etched, it should not be more than just enough to destroy the gloss of the polished surface. The specimen should be heated to a red heat in a blast lamp and allowed to oxidize in the open air until the gloss from the polished surface has just disappeared, when the entire sample should be cooled below a red heat as quickly as possible by holding it in a blast of cold air. It is often more difficult to get good results with the relief polish than with the heat etching. The specimen should be examined frequently with the microscope during the polishing operation, and as soon as a good relief is obtained the polishing should be stopped, for a relief once developed can be easily de-

stroyed by polishing a little too long. In some cases the relief polish might be followed to good advantage by the heat etching, giving better results than could be obtained from either used alone.

After a specimen has been etched sufficiently, and has been shown by a preliminary examination under the microscope to be in the condition in which it is desired, it should be mounted permanently on a slide. The etched surface is very delicate, and if it is attempted to preserve the specimens loose, even though they are packed in cotton, the liability of damage to the etched surface is great. They are best preserved by mounting them on a regular microscope slide by means of sealing wax. In order that the entire surface of the specimen may be in focus, it is necessary in mounting that its surface be kept perfectly parallel with the surface of the slide on which it is mounted. This is done by means of the device shown in Fig. 1, which can be

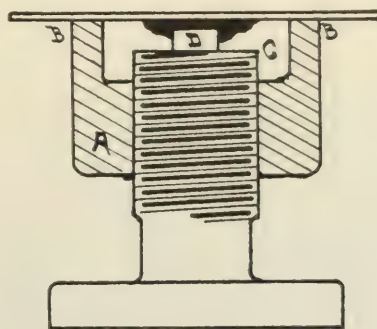


Fig. 1.—Mounting device for specimens.

made in any machine shop. By turning the circular ring A, the surfaces B and C can be separated any distance desired and yet always remain parallel to each other, if the instrument has been properly made. The specimen D is laid polished surface down on the face C, the ring A is turned until a slide laid on B just clears the specimen, a few drops of hot wax are then dropped on the back of the specimen or on the center of the slide, and the slide is pressed down against the face of B until the wax is cold.

After the preparation and mounting of the specimen it is ready for examination under the microscope. For this purpose any microscope can be used which can be supplied with an apparatus for vertical illumination, descriptions of which can be obtained from any standard work on metallography. The instrument used in this investigation was the Leitz metallograph, supplied with eye-pieces and objectives giving magnifications of 65, 200, 325 and 550 diameters. Practically all of the work was done with the two lower magnifications, the larger ones being used only occasionally when a sample was found in which the raw materials had been ground exceedingly fine.

Whenever possible the samples should be filed away for future reference, but where this is impossible, or where records are wanted for any other purpose, recourse may be had to photography, which will reproduce the appearance of the samples in all of their detail. In some ways the photomicrograph is of more value

than the original sample as a record, since it makes easy the comparison of one sample with another, or different magnifications of the same sample. The details of this process can be obtained from some book on photography or metallography.¹

A carbon treated in this manner and viewed under the microscope has an appearance similar to Figs. 2 and 3. In these the individual grains can be distinguished readily, the former being magnified 65 diameters and the latter 200 diameters. The problem now before us is to find some means of distinguishing between the different individual grains when some are of one material and some are of another. This was accomplished by studying pure samples of the different raw materials that enter into the make-up of the carbons. As has been shown in the list of raw materials, the most important of these are petroleum coke, retort carbon, artificial graphite and natural graphite, varying in importance in the order named. These will be taken up and discussed in this order.

Petroleum Coke.—Petroleum coke is the residue left in the still in the refining of crude oil. As obtained from the oil refineries, it is a black, porous carbonaceous mass, still containing a considerable percentage of oil, which must be removed by calcining before the coke can be used in the manufacture of carbons. While the mass is visibly porous, from its nature and origin one would suspect this porosity to extend beyond the limits of visibility, and as a matter of fact, it does. Fig. 4 is a section of petroleum coke magnified 65 diameters. This shows to good advantage the large pores in the mass, and the cellular nature of the finer part of the structure. Fig. 5 shows the same section under a magnification of 200 diameters. Here it can be seen that the porosity of the material still persists up to the limits of this magnification, giving the surface a peculiar striated appearance, due to the numerous fine pores throughout the mass of the material. This striated appearance is characteristic of petroleum coke, and can easily be detected and recognized wherever this material is found. Numerous samples of petroleum coke have been examined from different sources, that had received all sorts of different treatment, and none were found in which this peculiar characteristic striated appearance could not easily be developed and recognized.

Fig. 6 shows a section of a carbon rod known to be made from petroleum coke, magnified 65 diameters, showing the structure of the body of the carbon. Fig. 7 is the same section under a magnification of 200 diameters, showing the characteristic striated appearance developed in the particles of petroleum coke. Figs. 8 and 10 compared with Fig. 6 show what varied appearances may be met in the shape of the individual grains and the structure of the body of the carbon, yet all, under the higher magnification, show the same characteristic appearance of petroleum coke, as seen in Figs. 7, 9 and 11.

¹ For greater detail concerning the apparatus and operations mentioned consult any of the following books: Gulliver, *Metallic Alloys*; Law, *Alloys and Their Industrial Application*; Osmond and Stead, *The Microscopic Analysis of Metals*; Howe, *Iron, Steel and Other Alloys*; Ruer-Mathewson, *Introduction to Metallography*.

Retort Carbon.—Retort carbon is the carbon deposited in the flues leading from the retorts in a coal gas bench. Most retort carbon is found as a heavy steel-gray mass with a granular structure. The mass may vary considerably in density and porosity in different parts, and may be contaminated with more or less soot, but it is of a fairly uniform granular structure throughout. A second form is found in the shape of nodules, which have been deposited in successive layers, and the grains of carbon are usually smaller than in the granular variety. Fig. 12 shows a section of granular retort carbon under a magnification of 65 diameters; Fig. 13 shows a section of nodular retort carbon under the same magnification. In the former the uniform body of the material is shown, while in the latter the successive layers from which the nodules are built up are readily distinguished. Under a higher magnification both varieties show practically the same structure, a somewhat roughened, finely pitted surface, apparently made up of very fine granules, as shown in Fig. 14, where the same sample as shown in Fig. 12 is shown under a magnification of 200 diameters. This structure is not changed at a still higher magnification as is shown in Fig. 15, which is a sample of retort carbon under a magnification of 325 diameters. This is the characteristic structure of retort carbon. As in the case with petroleum coke, wide variation may be met in shape of the individual grains and the structure of the body of the carbon, as can be seen in Figs. 16, 18 and 20, but under the higher magnification all show the characteristic pitted surface, as seen in Figs. 17, 19 and 21.

Graphite.—The presence of graphite in a carbon, if to any appreciable extent, can be detected by the general appearance of the carbon and by the specific gravity. Carbons made from petroleum coke and retort carbon are not liable to have a specific gravity higher than 2.05, and many do not go above 2.00, while graphite has a specific gravity of 2.25–2.30. The amount of ash in the sample is also an indicator. A carbon made from a good grade of petroleum coke should not exceed 0.25–0.75 per cent. of ash, the latter being a high figure. A good grade of retort carbon will run from 1.00 to 2.00 per cent., with occasionally 2.50 per cent. If artificial graphite be present in the carbon, these figures may not be changed very much, for the better grades of artificial graphite do not have a very high ash content. It is probable, though, that one of the lower grades would be used, which would result in an appreciable increase in the ash content. If natural graphite were used, the difference would be still more marked, unless an exceptionally pure graphite were used.

Artificial Graphite.—Artificial graphite, being a manufactured product obtainable from several different sources, does not show a distinctive structure such as characterizes petroleum coke and retort carbon. No samples of artificial graphite have been found thus far that possess any distinctive characteristic markings of their own. Fig. 22 shows a section from a block of Acheson graphite, presumably made from petroleum coke. Fig. 23 is a section from another

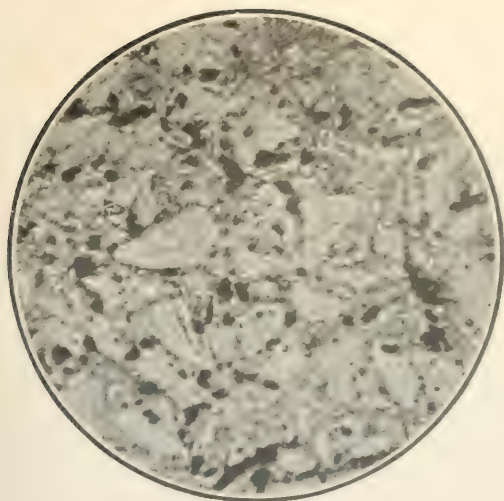


Fig. 2. 65.
Carbon sample showing structure and individual grains.
Heat-etched.

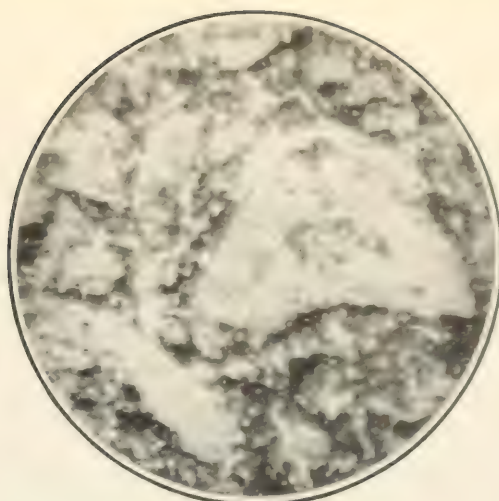


Fig. 3. 200.
Carbon sample showing structure and individual grains.
Heat-etched.

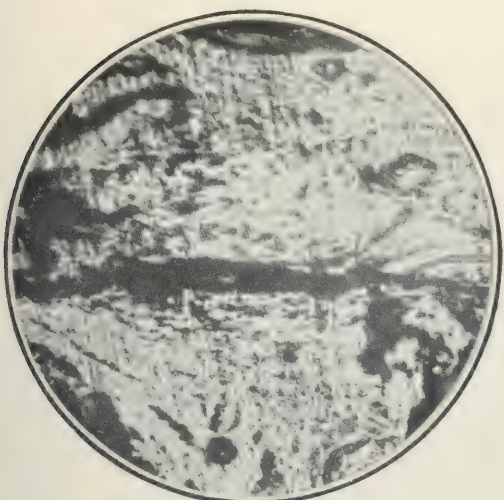


Fig. 4. 65.
Section of petroleum coke. Relief pol'sh.

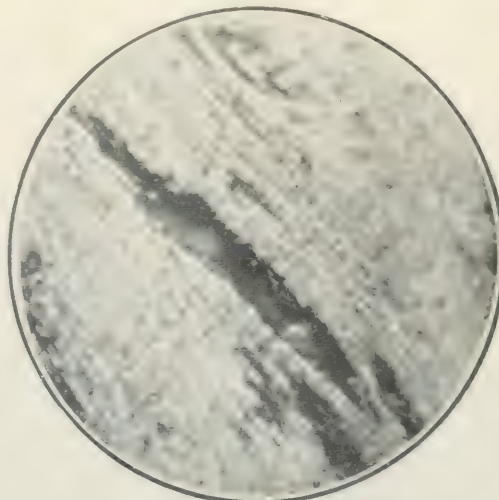


Fig. 5. 200.
Section of petroleum coke. Relief polish.

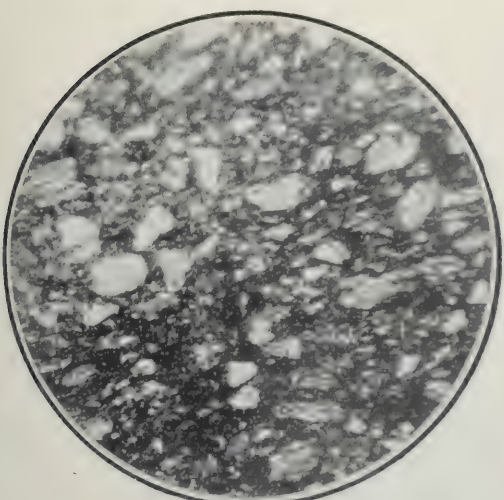


Fig. 6. 65.
Carbon rod showing individual grains of petroleum coke.
Heat-etched.

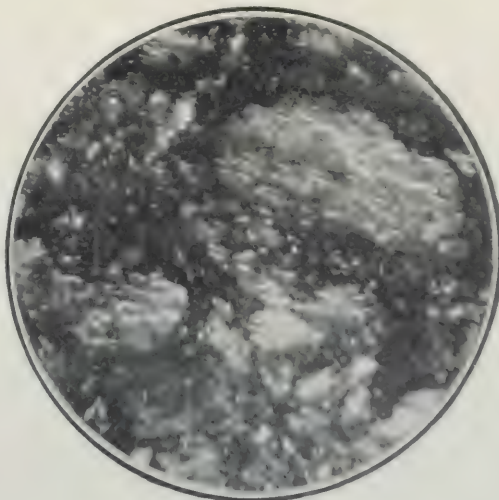


Fig. 7. 200.
Fig. 6 under higher magnification. Heat etched

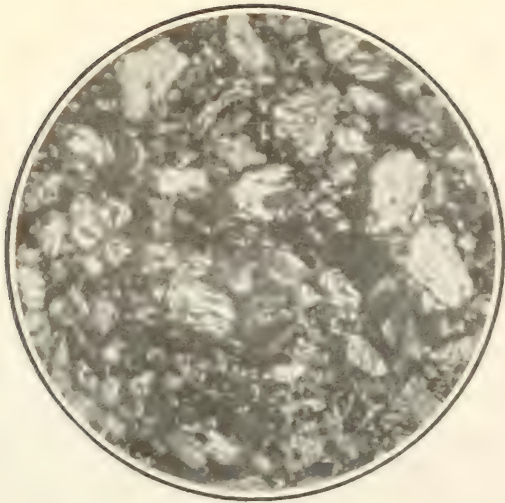


Fig. 8. $\times 65$.
Carbon rod showing individual grains of petroleum coke.
Heat-etched.

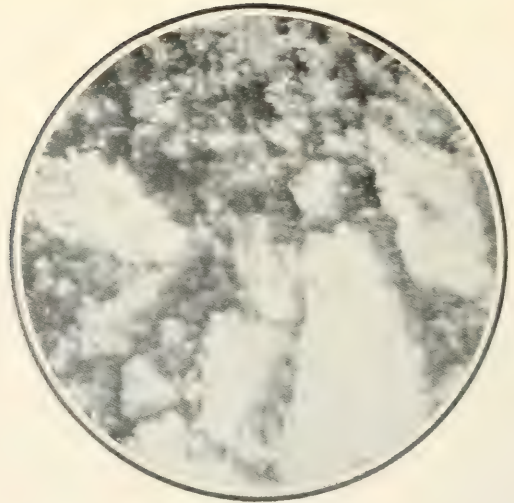


Fig. 9. $\times 200$.
Fig. 8 under higher magnification. Heat-etched.

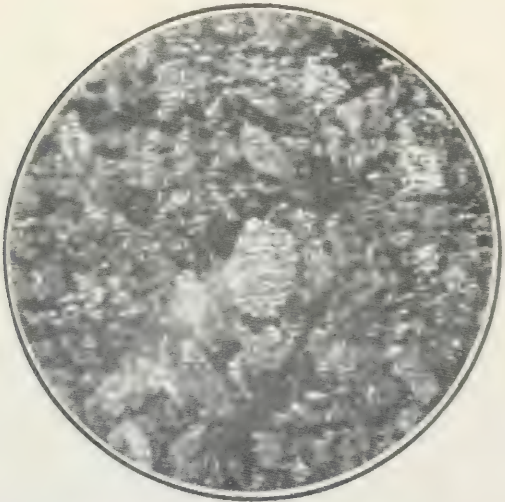


Fig. 10. $\times 65$.
Carbon rod showing individual grains of petroleum coke.
Relief polish.

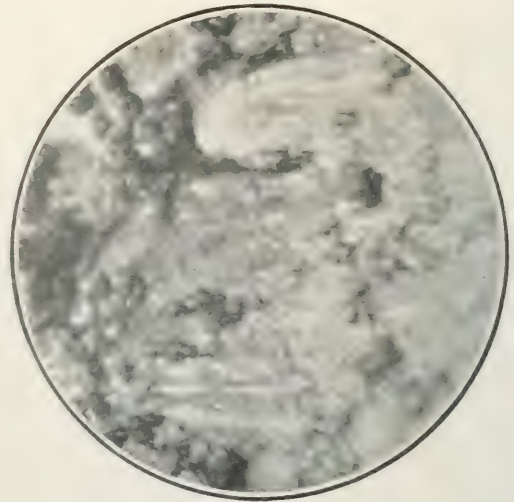


Fig. 11. $\times 200$.
Fig. 10 under higher magnification. Relief polish.

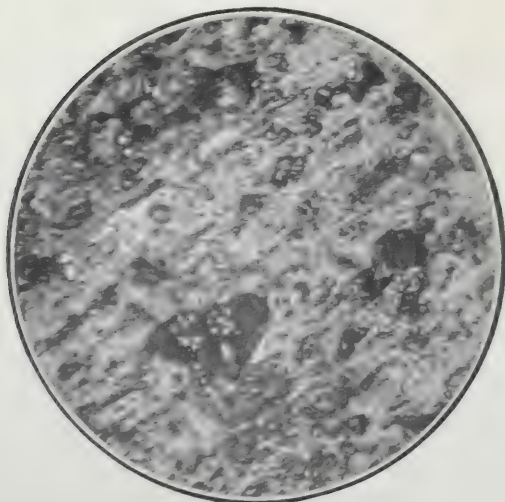


Fig. 12. $\times 65$.
Section of granular retort carbon. Relief polish.

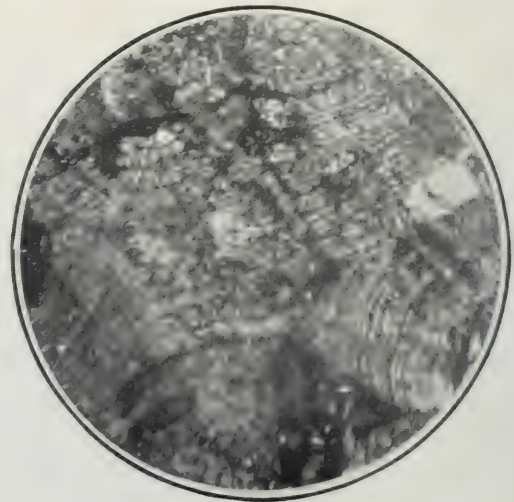


Fig. 13. $\times 65$.
Section of nodular retort carbon. Relief polish.

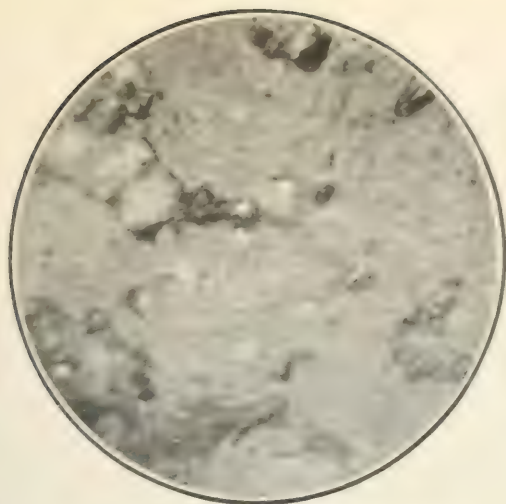


Fig. 12 under higher magnification. Relief polish.

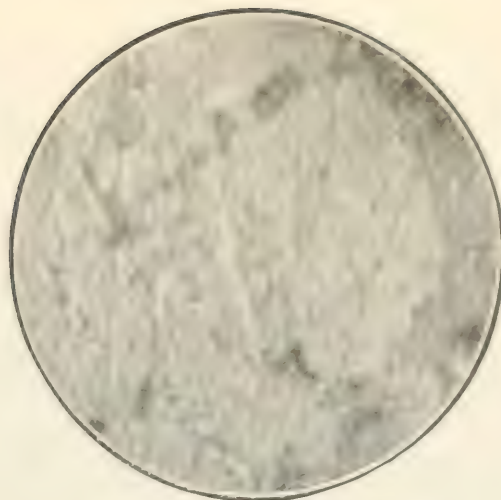


Fig. 13 under higher magnification. Relief polish.

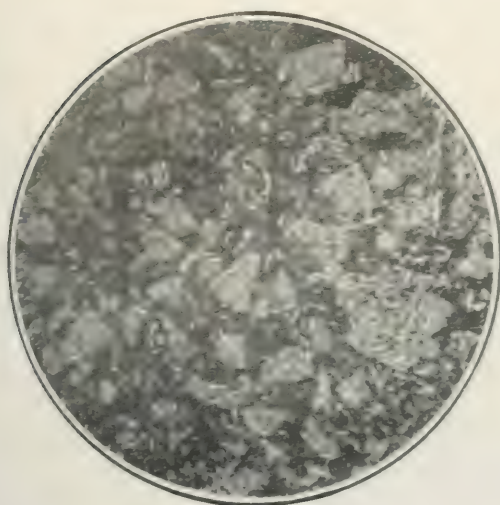


Fig. 14 Carbon showing individual grains of retort carbon. Relief polish.

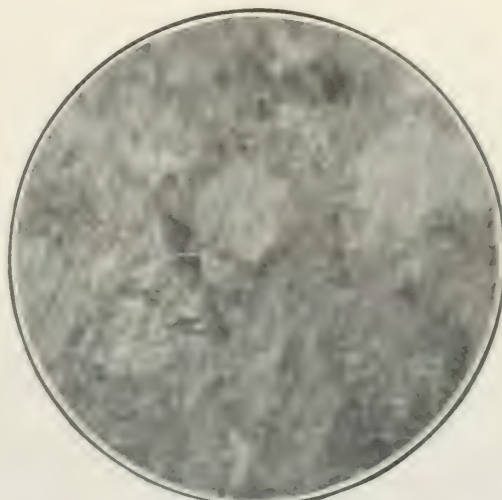


Fig. 15 under higher magnification. Relief polish.

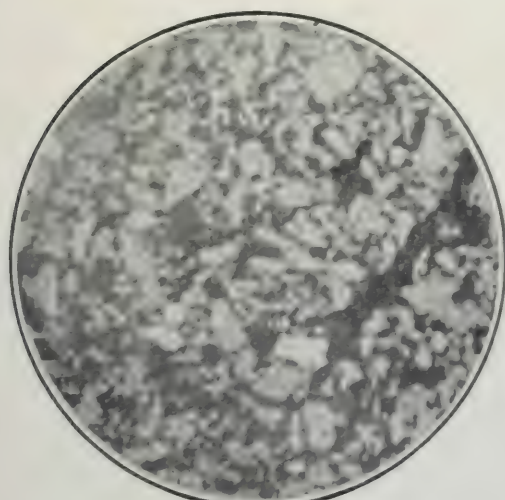


Fig. 16 Carbon showing individual grains of retort carbon. Heat-etched.



Fig. 17 under higher magnification. Heat-etched.

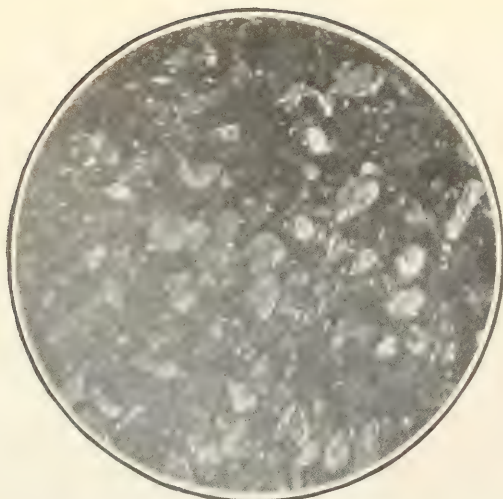


Fig. 20. $\times 65$.
Carbon showing individual grains of retort carbon. Heat-etched

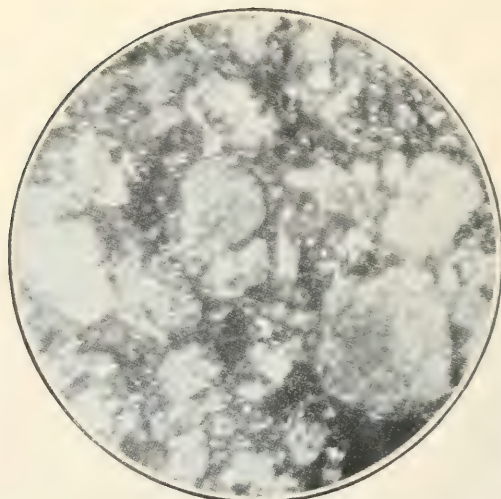


Fig. 21. $\times 200$
Fig. 20 under higher magnification. Heat-etched.

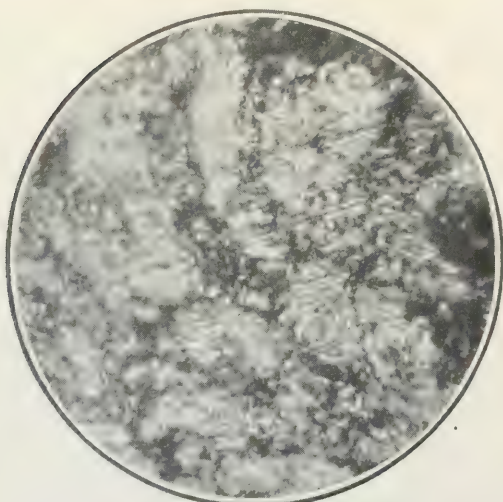


Fig. 22. $\times 200$.
Section of Acheson graphite. Heat-etched.

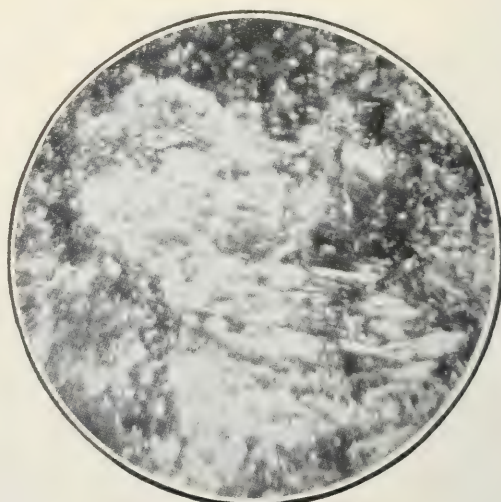


Fig. 23. $\times 200$.
Section of Acheson graphite. Heat-etched.

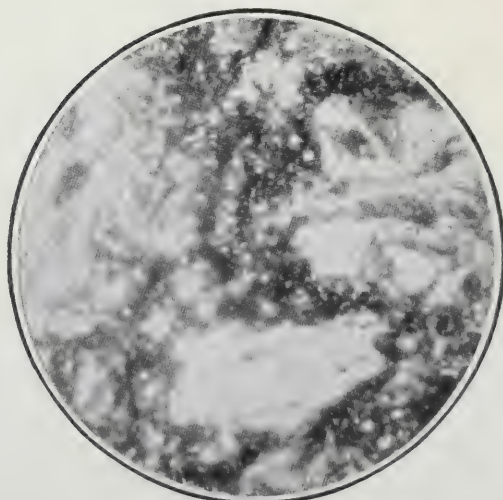


Fig. 24. $\times 200$.
Sample containing petroleum coke and artificial graphite. Heat-etched.

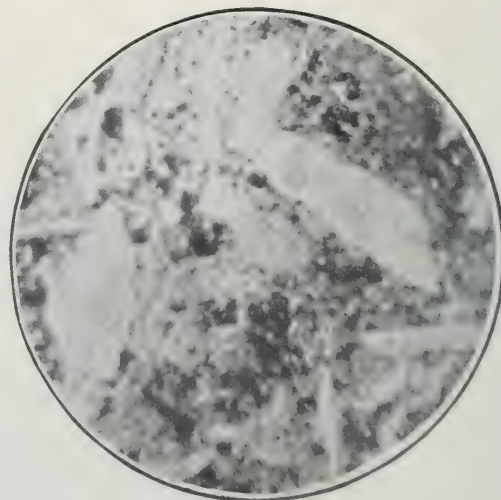


Fig. 25. $\times 200$.
Sample containing retort carbon and artificial graphite. Relief polish.

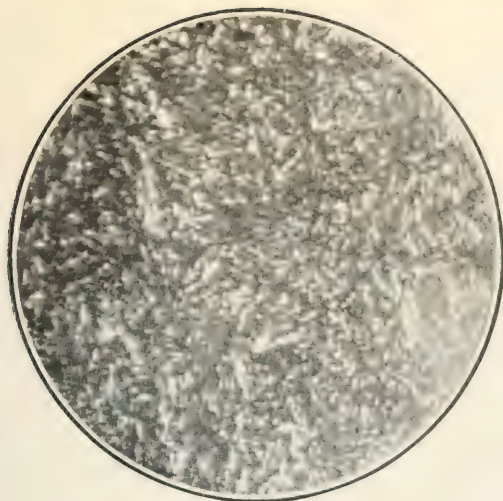


Fig. 26 65.
Carbon from fine natural graphite. Heat-etched

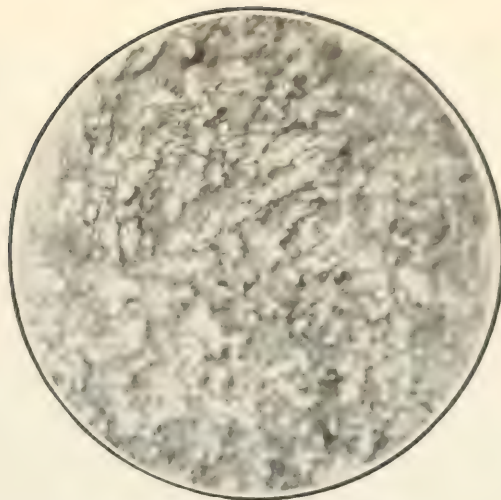


Fig. 27 200.
Fig. 26 under higher magnification. Heat-etched.

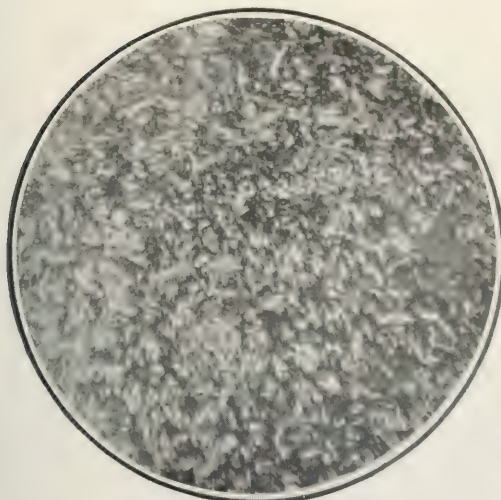


Fig. 28 65.
Carbon from larger natural graphite. Heat-etched.

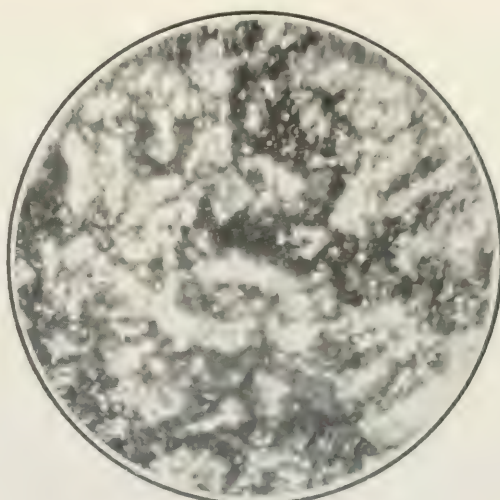


Fig. 29 200.
Fig. 28 under higher magnification. Heat-etched.

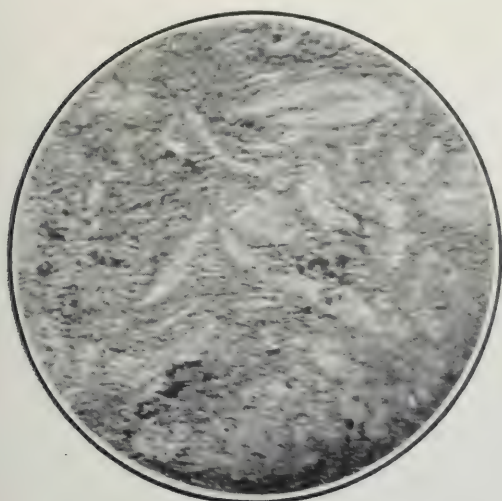


Fig. 30 325.
Carbon from larger natural graphite. Relief polish.

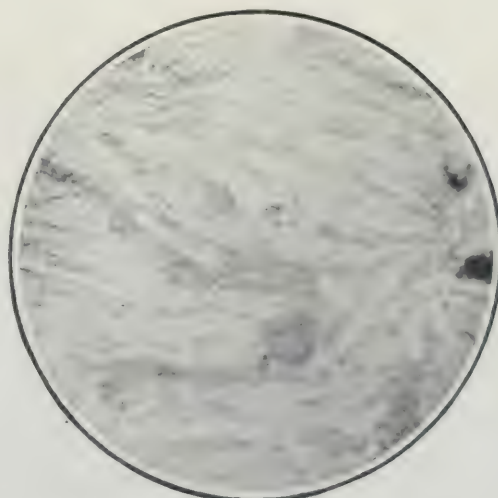


Fig. 31 65.
Carbon from coarse natural graphite. Relief polish.

piece of Acheson graphite that plainly shows its origin by its characteristic striated appearance. The question immediately presents itself, Why should one of these samples show no distinctive markings, and the other show them so plainly? Is this second sample a case of incomplete conversion, or is this retention of form analogous to a pseudomorphous crystal? Samples similar to the latter are not at all hard to find; as a matter of fact, they seem to be more numerous than the former.

So far, artificial graphite has shown no characteristics by which it can be distinguished from other materials under the microscope. The samples shown in Figs. 24 and 25 contain more or less graphite along with the other constituents, but one is not able to pick out the individual particles as can be done with the petroleum coke and retort carbon, and since, as is stated above, artificial graphite can be made from any of the different forms of amorphous carbon, we are liable to find samples of artificial graphite which still retain more or less of the appearance of any of the possible original materials. A full and careful study of the graphites obtained from the different commercial varieties of amorphous carbon will be required before one can say with any assurance that these forms of graphite can be identified, and distinguished one from another.

Natural Graphite.—The natural graphites are as a rule more or less of a flaky nature, with the flakes varying in size from an almost impalpable powder up to almost an eighth of an inch across. While the natural graphites do not have any very distinctive markings, after a little experience one can generally recognize them by the shape of the flakes. Figs. 26 and 27 show a sample of very fine natural graphite under magnifications of 65 and 200 diameters, respectively. Figs. 28 and 29 show a graphite with a slightly larger flake, under the same magnifications. Figs. 30 and 31 show flakes of still larger size, the former being enlarged 325 times, and the latter only 65 times. These last two samples are finished with the relief polish, while the other two are heat-etched. The different results produced by the two methods on similar materials is shown clearly.

Similarities and Differences.—Occasionally cases are found where particles of one material show an appearance similar to one of the other materials, and require considerable study and manipulation before they can be definitely identified as one or the other. The preparation of several specimens from each sample examined usually will enable one to avoid false conclusions in a case of this kind.

A nodular retort carbon, such as is shown in Fig. 13, may under some conditions appear very similar to the striated surface of petroleum coke. This can usually be detected by a higher magnification, which will develop to a greater extent the characteristic structure of the retort carbon, and will also aid in the identification by bringing out more clearly the almost perfect parallelism of the lines on the surface, which is much more perfect than is found in the striations of petroleum coke.

The striated appearance of the petroleum coke is

due to the presence of minute pores extending throughout the body of the material. If the section is cut so that its surface is perpendicular, rather than parallel, to the course of these pores, the surface will appear more or less pitted, similar to the characteristic structure of retort carbon, particularly under the lower magnifications. This can usually be detected without much difficulty by a higher magnification and specimens cut from other parts of the sample under examination.

A natural graphite in large flakes, if etched by heat, may show striations similar to petroleum coke, but this material can usually be detected by the shape of the flakes, as shown in Figs. 29, 30 and 31.

With a little experience, one can become familiar with these similarities and differences, so that the identification of the different materials can be accomplished without much difficulty.

Optical Analysis.—The next step after the identification of the constituents of the carbon is the determination of the quantities in which the different constituents are present. When the materials have been ground very fine, this is a difficult matter, but if the particles are not too small, so that their outlines can be definitely determined, fairly accurate results can be obtained. For this purpose, the methods of optical analysis used in petrography for the analysis of rocks can be used.

It has been determined¹ that the sum of the diameters of a large number of adjacent particles, measured in a straight line, bears the same ratio to the total length of the line from outside to outside of the first and last particles, as the volume of these particles is to the total volume of the material; in other words, the quotient obtained by dividing the total length of the line into the sum of the diameters of the particles touching the line and measured on the line, gives the percentage by volume of the whole, occupied by those particles. For this purpose the sample in question is put under the microscope at a magnification sufficient to clearly distinguish all of the individual particles, using a micrometer eye-piece, preferably one with cross hairs unless the scale of the micrometer has a line drawn lengthwise through it, as some do have. This will give the field an appearance like that shown in Fig. 32. The hair line serves as the straight line across the surface of the specimen, along which the measurements are to be made. Those portions of the line are measured which lie on the particles whose percentage is sought. Whatever may be the size or shape of the particles encountered, that portion of the line is measured that lies on the surface of all the particles under the scale of the micrometer, and note is made of the total length of the micrometer scale, and of the sum of all the diameters of the particles as measured along the straight line. Other portions of the specimen are then measured in the same way until the total distance measured over is at least 100 times the diameter of the largest particle encountered. The greater the total length measured, the greater the accuracy of the results, and,

¹ Rosiwal, *Verh. Wien. Geol. Reichsanstalt*, **32**, 143 (1898); Williams, *Am. Geol.*, **35**, 40-43 (1905); *Quantitative Classification of Igneous Rocks*, by Cross, Iddings, Pierson and Washington, 204.

if possible, several different specimens of the same material should be used in order to get a better average. When the desired number of measurements have been made, the sum of the diameters measured; times 100,

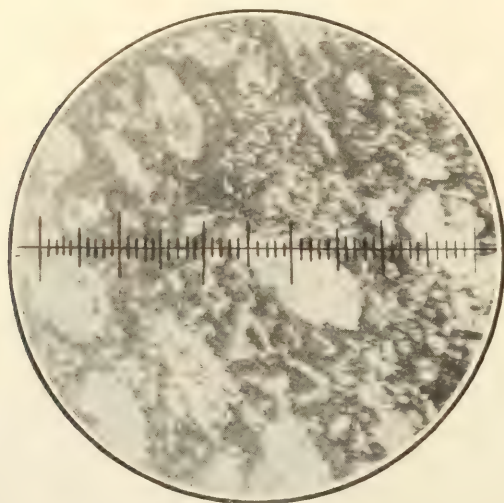


Fig 32 65.
Specimen under micrometer eye-piece ready for measurement.

divided by the total distance measured over gives the percentage by volume occupied by the particles measured. By this method, several different constituents may be determined at one time simply by having separate columns to add the diameters of the different particles measured. When the material is made up of two or more constituents, it requires more work to get the desired results, because it usually requires a higher magnification to distinguish one constituent from another by their characteristic markings than it does to simply distinguish the individual particles from each other; for this reason the apparent diameters of the particles as measured will be greater, and a greater number of measurements will be required in order to secure the desired accuracy.

When the percentage by volume has been determined the percentage by weight, if desired, can be calculated from the density of the whole mass and that of the material in question.¹

The accuracy of this method as applied to materials of this kind is not as great as might be desired, but with care, results can be obtained that have sufficient accuracy to make them of considerable value. The first precaution to be observed is to secure as fair an average as possible by making a large number of measurements from as many different samples of the material in question as can be obtained. The fineness to which the constituents entering into the carbon have been pulverized has considerable effect on the accuracy of the results, for if the particles are exceedingly small, it is difficult to obtain a polished section in which the outlines of the grains are clear and definite. For this reason, the results as obtained are always liable to be more or less below the true values, owing to the fact that it is difficult, in making the measurements, to find and include all of the very fine particles. Low results

¹ Methods for the determination of the density of carbon can be found in the article referred to in Note 1.

may also be expected to a certain extent if the section has been prepared by heat etching rather than by the relief polish, since the burning destroys to a greater extent the original outline of the grains.

Specimens of known composition have shown results differing from the calculated contents by only one per cent., while in other cases the difference was as high as four or five per cent., depending on the success with which the sections measured were prepared, the size of the grains, and the definiteness of their outline. The difficulties encountered with very small grains can be only partially avoided by higher magnification. This will of course make the grains more easily distinguished, but they will still lack definiteness of outline. As with all the other operations, a little experience will give one the ability to make the measurements fairly readily.

Conclusion.—These methods of identification and analysis should prove of some value to the manufacturers and users of carbons of various kinds, particularly so of dynamo and motor brushes, the manufacture of which must be very closely followed in order to secure a uniform product, and a systematic study of the structure and body of the different materials should lead to a marked improvement in their quality and wearing properties.

The outline of this subject as presented here still leaves much to be desired, but it is hoped that sufficient results have been shown to prove themselves of use, and it is hoped that the field may soon be broadened, and further results added to those already obtained.

MORGANTOWN, W. VA.

[CONTRIBUTION FROM RESEARCH DEPARTMENT, THE AMERICAN ROLLING MILL CO., MIDDLETOWN, OHIO.]

THE DETERMINATION OF OXYGEN IN IRON AND STEEL.

By ALLERTON S. CUSHMAN, Director of Institute of Industrial Research.

Received April 22, 1911.

The determination of oxygen in iron and steel has not received sufficient attention in the United States. The text-books on steel works analyses, which are in common use in this country, do not include methods of analysis for oxygen content of irons and steels. This is probably due to the fact that in the ordinary steel-making processes ferro-manganese can be freely used, so that it is assumed that the percentage of oxygen in the steel rarely reaches or exceeds the danger point. As a matter of fact, steel often carries much more oxygen than it should, as can be seen by referring to Table II.

In the manufacture of iron of very high purity in basic open-hearth furnaces the oxygen content has to be very carefully watched, or the product may be overburned and contain an excess of oxide and dissolved oxygen.

A number of methods for the determination of oxygen have been proposed, among which may be mentioned: (1) Heating the sample in a stream of dry chlorine; (2) dissolving the sample in special solvents such as copper sulphate or bromine; (3) combustion of the sample in the form of borings in pure dry hydrogen.

The latter method, which is due to Ledebur,¹ is the only one that has proved reliable. In Ledebur's original method, the sample is given a preliminary combustion in pure nitrogen in order to burn off the last traces of impurities and to get rid of all hydrocarbons, as well as adsorbed oxygen on the surface of the particles of the sample. If the preliminary heating in nitrogen is dispensed with, the results will be slightly higher, but it is probable that for general work sufficiently accurate results can be obtained if the sample is carefully prepared for the combustion in hydrogen.

SAMPLES.

The samples should consist of fine borings or shavings from a milling machine. The drill or machine tool should be scrupulously clean and free from all traces of oil or dirt, and should be geared to run slowly so as not to heat the sample while it is being cut. Lack of careful attention to this point will lead to high results, owing to surface oxidation of the fine particles of the drillings.

APPARATUS.

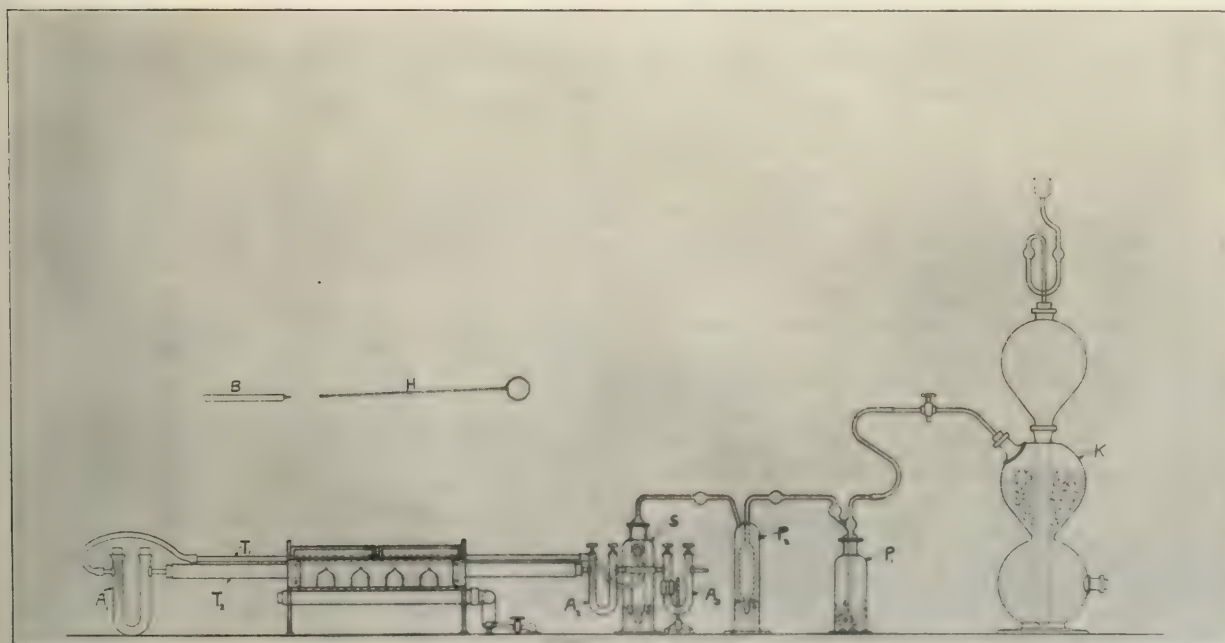
The apparatus used in making the oxygen determination is shown in illustration B-740.

A one-gallon Kipp generator is used for generating the hydrogen. It should be charged with drillings

as shown in the figure. It passes first over stick potash, and next through a 30 per cent. potash solution. This solution in the second bottle should be renewed as soon as it shows a tinge of yellow, due to the appearance of sulphides. The hydrogen next passes through concentrated sulphuric acid to dry it, and then enters a silica tube with $\frac{1}{4}$ " bore, 30" in length, which contains a 6" roll of platinum gauze. The $\frac{1}{4}$ " tube lies on top of a 1" \times 30" fused silica tube contained in a suitable 12" gas blast furnace.

The object of the preliminary heating over platinum foil is to free the hydrogen from the small quantity of oxygen which it always contains. If this precaution is not taken, the results will be too high. The water formed in the small-bore silica tube is caught in a "U" tube shown in the figure, which contains phosphoric anhydride opened up with glass wool. This drying tube has rubber stoppers. The connection is made with pure gum tubing and is permanent, the sample being introduced from the opposite end of the combustion tube.

Blanks should be run from time to time to make sure that the apparatus is in good order and everything working properly. Samples should not be introduced into or removed from the combustion tube when it is more than hand-hot, but silica tubes may be



Denotations:

K—Kipp generator.
P₁—Potassium hydrate sticks.
P₂—Potassium hydrate solution.
S—Sulphuric acid conc.
T₁— $\frac{1}{4}$ " bore silica tube.
T₂—1" bore silica tube.

A₁—U-tube phosphoric acid.
A₂—U-tube phosphoric acid weighed.
A₃—U-tube phosphoric acid trap.
B—Platinum boat.
H—Hook of $\frac{1}{8}$ " copper wire.

of pure iron or mossy zinc, and dilute hydrochloric acid (1:1). Steel turnings should not be used in the generator, as the object is to generate the purest possible hydrogen. Hydrochloric is preferable to sulphuric acid. After its formation the hydrogen is purified and dried by passing through the usual train

quickly cooled with perfect safety by turning off the gas and allowing the cold air blast to play on the tube.

METHOD.

Twenty to thirty grams of finely divided borings are weighed into a platinum or silica boat $\frac{1}{2}$ " \times $\frac{1}{2}$ " \times 6". The boat with its charge is quickly in-

¹ "Leitfaden für Eisenhüttenlaboratorien," Vieweg und Sohn, Braunschweig, 6 Auflage, 1903, S. 122.

serted in the combustion tube and pushed to the middle zone by means of a rod of suitable length. The stream of hydrogen should be passing freely when the tube is opened for the insertion of the sample. After the stopper is replaced, the weighing tube and guard tube are finally connected with pure gum tubing. The weighing tube is a 4" "U" tube, with ground glass stoppers, containing phosphoric anhydride opened up with glass wool. The guard or trap tube is similarly charged and is intended to prevent the drawing back of moisture from the air of the laboratory. After the apparatus is all connected and in good order, the pure dry hydrogen should be allowed to sweep through a few minutes until all air is removed from the entire system. The gas is then lighted, the blast turned on and the temperature quickly run up to a bright red heat, about 850° C. This heat is maintained for thirty minutes, while the hydrogen is passing through the apparatus at the brisk rate of about 100 cc. per minute. After the combustion is completed the gas is turned off the furnace, leaving the blast playing upon the hot tube. The stream of hydrogen should continue to pass until the tube is cool enough to bear the hand upon it.

Immediately after the tube is cool enough, the hydrogen is shut off and the weighing tube, with its guard tube, disconnected and connected with a suitable aspirator, so as to suck out the hydrogen gas and replace it with dry air. A suitable aspirator consists of a one-gallon aspirator bottle filled with water. The upper tubulure of the bottle is guarded with a calcic chloride tube to which the weighing tube is connected. Another calcic chloride tube is attached at the same time to the other end of the main guard tube to prevent the phosphoric anhydride from being wetted by the moisture of the laboratory air.

The aspirator may be roughly calibrated by allowing about 500 cc. of water to run out of the lower tubulure of the aspirator. A sufficient quantity of perfectly dry air is drawn through to thoroughly displace all the hydrogen. After all is ready, the weighing tube is closed by its glass stopcocks, disconnected from its guard tube and placed in a desiccator for fifteen minutes before being weighed. Eight-ninths of the increased weight of the tube is oxygen. The blanks on the apparatus establish the average correction to be subtracted from the weight found. The correction on an apparatus in good order should not exceed three milligrams. On damp days the blank is usually a little higher than when the air is dry.

In charging the weighing tube with phosphoric anhydride and glass wool, take care to remove any specks of phosphoric acid from the upper portions of the tube. The following points should be given careful attention in order to attain the highest degree of accuracy.

Samples must be clean, absolutely dry and free from oil. They should be cut, preferably with a milling machine tool running at a low rate of speed. The samples must not heat in cutting. Sheet samples are first cleaned from oxide on an emery wheel, avoiding heating as much as possible. The sheet should be milled on the edge.

Whenever possible, samples should be cut from bars which are first cleaned by a superficial cut with the milling tool.

Extreme care must be taken in the preparation of the sample.

The entire apparatus must be kept to the top notch of cleanliness, tightness and general good order. Blanks should be run frequently. Analyses should be in duplicate whenever the results are to be used as a basis for specification. The most extreme care should be taken to exclude all oxygen from the sample and apparatus except that which it is the object of the method to determine. When pure iron is worked on, the silver-white iron residues from the boat should be reserved for charging the Kipp hydrogen generator.

In the following table are given a number of oxygen determinations:

TABLE I.

Material.	Sili- con.	Sul- phur.	Phos- phorus.	Car- bon.	Manga- nese.	Nitro- gen.	Oxy- gen
American Ingot Iron (01107) (Sheet).....	0.003	0.021	0.002	0.01	Trace	0.0050	0.027
American Ingot Iron (02007) (Sheet).....	0.003	0.018	0.004	0.015	0.020	0.0060	0.014
Electrolytic Sheet Iron, by Elec- trolysis.....	0.000	0.001	0.005	0.006	0.000	0.0030	0.032
American Ingot Iron Chain (Link).....	0.008	0.022	0.008	0.015	0.025	0.0063	0.032
Norway Iron Chain Link, 100 years old.....	0.019	0.007	0.032	0.050	0.000	0.0047	0.058
Puddled Iron 1- 1/2" Bar broke in service.....	0.056	0.047	0.140	0.065	0.070	..	0.855
Norway Iron Piano Wire.....	0.007	0.006	0.012	0.025	0.020	..	0.050
Puddled Iron Chain Link.....	0.075	0.009	0.072	0.010	0.010	..	0.145
Puddled Iron Sheet.....	0.077	0.020	0.074	0.015	0.010	..	0.283

TABLE II.

In this table a number of oxygen determinations in steels are given. These results were obtained by Romanoff¹ working with the Ledebur method.

No.	Carbon.	Phos- phorus.	Man- ganese.	Sul- phur.	Oxy- gen.	Specific gravity.
496.....	0.107	0.04	0.57	0.03	0.19	7.79
478.....	0.25	0.01	0.54	0.03	0.15	7.85
572.....	0.25	0.02	0.55	0.04	0.26	7.72
516.....	0.10	0.04	0.50	0.07	0.11	7.92
503.....	0.10	0.08	0.55	0.06	0.25	7.84
526.....	0.095	0.02	0.37	0.06	0.22	7.78
540.....	0.10	0.04	0.48	0.07	0.16	7.82
547.....	0.095	0.04	0.49	0.05	0.11	..
550.....	0.105	0.05	0.49	0.03	0.14	..
551.....	0.09	0.06	0.32	0.04	0.16	7.87
553.....	0.095	0.08	0.39	0.04	0.13	7.80
555.....	0.10	0.05	0.44	0.03	0.13	7.87
570.....	0.095	0.02	0.03	8.08
581.....	0.105	0.06	0.46	..	0.09	7.97
583.....	0.10	0.04	0.42	0.03	0.02	8.08

THE DETERMINATION OF MANGANESE BY THE SODIUM BISMUTHATE METHOD.²

By W. F. HILLEBRAND AND WILLIAM BLUM.

In a recent paper on this subject by Brinton,³ the author concludes that an empirical factor is necessary in the bismuthate method if the permanganate solution

¹ Stahl und Eisen, March 15, 1899.

² Published by permission of the Director of the Bureau of Standards.

³ This Journal, 3, 237-8.

is standardized by means of sodium oxalate or an iron ore. As all the experience at the Bureau of Standards indicates that no such empirical factor is necessary, the data given by Brinton were examined, leading to the following observations: The theoretical factor for the ratio $5\text{Na}_2\text{C}_2\text{O}_4 : 2\text{Mn}$ is 0.16397 and not 0.16024 as stated by Brinton, while the ratio $5\text{Fe} : \text{Mn}$ is correctly stated, *viz.*, 0.1967. If the incorrect factor was used by him, the results given by him in the last two lines of Table I are too low, while if the correct factor was used, the empirical factor necessary to increase these results to the values found with MnSO_4 as a standard should be 0.1694, instead of 0.1656 as stated.

Recalculation of his results upon the former assumption led to the following values for manganese:

Bureau of Standards sample No. and name.	18—Acid open-hearth. 0.1 C.	102—Bessemer. 0.4 C. Renewal.	19—Acid open-hearth. 0.2 C.	13—Basic open-hearth. 0.6 C.	24—Vanadium steel.
Bureau of Standards averages...	0.412	0.916	0.760	0.568	0.669
Found with MnSO_4 as primary standard.....	0.410	0.912 ¹	0.757	0.557	0.663
	0.411	0.910 ¹	0.758	0.562	0.665
Found with $\text{Na}_2\text{C}_2\text{O}_4$ as primary standard, using factor 0.16024..	0.397	0.892	0.732	0.539	0.642
	0.398	0.890	0.733	0.544	0.644
Found with $\text{Na}_2\text{C}_2\text{O}_4$ as primary standard, using factor 0.16397..	0.406	0.903	0.749	0.552	0.657
	0.407	0.901	0.748	0.557	0.659

Consideration of the corrected values in the last two lines shows that they are uniformly about one per cent. lower than those found with MnSO_4 as a standard, which in turn are slightly below the Bureau of Standards averages. The question then arises whether these figures are sufficient to justify the recommendation of the empirical factor 0.1656; *i. e.*, addition of 1.0 per cent. to the value derived from sodium oxalate. This factor would depend upon (a) the purity and accurate standardization of the MnSO_4 solution; and (b) the assumption that the general averages given by the Bureau of Standards are accurate to 1 per cent. of their value. It is to be noted that impurities such as iron, calcium or magnesium in the manganous sulphate used would be included in the standardization both as sulphate and pyrophosphate, and would lead to too high results in the Mn values of the permanganate and of the steels.

The following test was applied at this Bureau to determine whether the bismuthate method required the theoretical factor. A measured quantity of a filtered 0.03 N permanganate solution, standardized with sodium oxalate, was reduced with sulphurous acid, of which the excess was expelled. It was then treated by the bismuthate method under exactly the same conditions as were used in the regular determinations. If the reactions proceed according to the theory, the amount of ferrous sulphate oxidized should be equivalent to the original volume of permanganate taken. The results were as follows:

TABLE II.

	Cc. KMnO_4 reduced and oxidized	Cc. FeSO_4 added.	KMnO_4 equivalent to FeSO_4 .	KMnO_4 required for excess.	KMnO_4 equivalent to FeSO_4 oxidized.	Error, cc.
1.....	20	25	23.78	3.75	20.03	+0.03
2.....	18	25	23.78	5.80	17.98	—0.02
3.....	16	25	23.78	7.80	15.98	—0.02

It was therefore concluded that, within the limits of titration, this method is quantitative, and requires the theoretical factor. Additional evidence as to the correctness of this factor is found in the results on B. S. Standard Sample No. 25, a manganese ore, for which the sixteen values by eight chemists, using in all eight distinct methods, gave a mean of 56.36 per cent. Mn, with an extreme variation of less than one per cent. of the amount present. Of these results, the two by the bismuthate method were 56.33 and 56.50, one chemist using the theoretical factor and the other an empirically determined factor.

From the following table of summaries of manganese determinations on 16 Bureau of Standards steel samples, it may be seen that the mean of the colorimetric determinations in 14 samples is from 1 to 7 per cent. higher, and is in no case lower, than the general mean. The bismuthate results, on the contrary, approach much more closely to the general means, and especially to the averages of all results except the colorimetric. It may be noted that in every case the corrected values of Brinton agree very closely with the averages excluding colorimetric values.

Until an exhaustive comparative study of these methods, as applied to such materials, is made, it is impossible to fix the true manganese value of these samples more accurately than is expressed in the general averages. Since, however, the colorimetric methods as usually employed, involve the use of similar standards in which the manganese can be no more accurately determined, the colorimetric values are probably less independent than those obtained by other methods. In general, these samples are of use as manganese standards only in analyses of similar materials, of approximately equal manganese content; and in using them, due regard should be given to the probable accuracy of the general averages, as indicated by the order of agreement of the values from which they have been derived. On some of the more recent samples, *e. g.*, 9a, 11a, 22 and 23, the agreement between the various methods is quite satisfactory, and the means are probably correct to 1 per cent. of their value.

In conclusion, it may be stated that further work is necessary to establish the value of the various methods for manganese, for both high- and low-grade materials, this being one of the problems which this Bureau hopes to undertake as opportunity offers. Until such work is accomplished, it is doubtful whether the manganese content of low-grade materials can be ascertained with a greater accuracy than one per cent. of the amount present.

¹ Typographical error in original.

TABLE III.

Bureau of Standards sample.	8a—Bessemer, 0.1 C. Renewal.	9a—Bessemer, 0.2 C. Renewal.	10a—Bessemer, 0.4 C. Renewal.	11—Basic open-hearth, 0.2 C.	11a—Basic open-hearth, 0.2 C. Renewal.	12a—Basic open-hearth, 0.4 C. Renewal.	13—Basic open-hearth, 0.6 C.	14—Basic open-hearth, 0.8 C.	15—Basic open-hearth, 0.1 C.	16—Basic open-hearth, 1.0 C.	18—Acid open-hearth, 0.1 C.	19—Acid open-hearth, 0.2 C.	20—Acid open-hearth, 0.4 C.	21—Acid open-hearth, 0.6 C.	22—Bessemer 0.6 C.	23—Bessemer 0.8 C.
Bismuthate.....	0.531	0.915	0.897	0.451	0.615	0.407	0.548	0.636	0.512	0.396	0.392	0.735	0.478	0.547	0.712	0.785
Persulphate colorimetric...	0.548	0.928	0.937	0.476	0.620	0.437	0.589	0.678	0.547	0.435	0.423	0.780	0.510	0.573	0.715	0.782
Lead peroxide colorimetric	0.950	0.520	0.620	0.670	0.530	0.460	0.425	0.770	0.500	0.560
Ford ¹ Williams.....	0.525	0.920	0.908	0.470	0.615	0.407	0.580	0.670	0.522	0.412	0.411	0.753	0.469	0.557	0.702	0.765
Gravimetric (Ford, etc.)...	0.535	0.915	0.905	0.452	0.627	0.420	0.555	0.636	...	0.399	0.562	0.700	0.765
Noyes.....	0.894	0.436	0.533	0.631	...	0.385	0.539
Volhard.....	0.530	0.890	0.430	0.706	0.775
General average.....	0.536	0.918	0.916	0.464	0.620	0.419	0.568	0.654	0.528	0.414	0.412	0.760	0.486	0.559	0.708	0.775
Colorimetric average.....	0.548	0.928	0.940	0.487	0.620	0.437	0.597	0.676	0.543	0.443	0.424	0.778	0.508	0.570	0.715	0.782
Per cent. above general average.....	2.2	1.1	2.6	5.0	0.0	4.3	5.1	3.4	2.8	7.0	2.9	2.4	4.5	2.0	1.0	0.9
Average excluding colorimetric.....	0.531	0.914	0.901	0.449	0.619	0.414	0.549	0.638	0.519	0.396	0.403	0.746	0.472	0.551	0.704	0.771
Per cent. below general average.....	0.9	0.4	1.6	3.2	0.1	1.2	3.3	2.4	1.7	4.3	2.2	1.8	2.9	1.4	0.6	0.5

NOTE.—The number of determinations involved is indicated in each case by a small superior numeral.

A. One discordant determination omitted.

BUREAU OF STANDARDS, WASHINGTON, D. C.

CORRECTION.

THE DETERMINATION OF MANGANESE BY THE SODIUM BISMUTHATE METHOD.

By PAUL H. M.-P. BRINTON.

Dr. W. F. Hillebrand has kindly called my attention to an arithmetical error in my article on this subject, which appeared in the April number of THIS JOURNAL. My error in taking the factor 0.16024 instead of 0.16397 for the ratio $5\text{Na}_2\text{C}_2\text{O}_4 : 2\text{Mn}$ is easily explained, though by no means excused, by a glance at a five-place table of logarithms. 2 Mn are equal to 109.86, and for this number I carelessly took 0.03084 as the mantissa, instead of 0.04084. This error in no way influences the correctness of my empirical factor 0.1656, though it may diminish the necessity for the use of an empirical factor. It should also be understood that this error in logarithm does not call into question the iron content of the Sibley ore, as might at first appear. The Sibley ore was first compared with sodium oxalate by a series of standardizations, both standards being correctly calculated to terms of iron. These were perfectly concordant, and then the work with the Sibley ore was discontinued. The comparison of the titer obtained by sodium oxalate and that by manganese sulphate was then taken up, and it was here that the error in computation was made.

April 24, 1911.

A CONTRIBUTION TO THE KNOWLEDGE REGARDING LOEW'S LIME-MAGNESIUM RATIO.

By ROBERT STEWART.

Received Feb. 3, 1911.

A knowledge of the beneficial action of lime on agricultural soils is almost as old as the practice of agriculture itself. Its benefits were known to the old Romans and to the early Japanese and Chinese. The results obtained, however, were not always uniform and seemed to vary with, among other things, the nature of the lime used. Lime which was made from magnesian limestone seemed to have detrimental effects. The presence of the magnesium in the limestone was regarded as exerting a detrimental influence. Why this should be so has been attributed to several different causes. Davy and others have attributed it to the relative slowness with which the caustic magnesia is converted into the carbonate by the absorption of the carbon dioxide of the air. Thus it is generally assumed by agricultural writers that the presence of magnesia, in excess, in the soil is detrimental to plant growth.

In 1901, Löew¹ advanced the hypothesis that when the lime and magnesia were present in the soil in a certain ratio the toxic action of magnesia is not manifested. May,² working under the direction of Löew, furnished experimental evidence of the truth of Löew's contention and advocated the optimum ratio of lime to magnesia of 5 : 4 on the basis of molecular weights, or 7 : 4 on the basis of actual weight.

¹ Bureau of Plant Industry, U. S. D. A., *Bull.* 1.

² *Ibid.*, 1, 52 (1901).

According to these investigators the toxic action of magnesia is due to an excess of magnesia over lime; and therefore the only remedy is such an addition of lime as will re-establish a favorable, or better optimum, ratio.

J. W. Konovalow,¹ in 1909, reported some investigation on the relationship between lime and magnesia, which he obtained by a study of nutrient solutions with various crops as grown by water and sand culture. He found that the best ratios of lime to magnesia were 6.7 : 1 and 3.3 : 1.

About the same time, Löew,² in a plea for including the determination of magnesium in soil analysis, claimed, among other things, that in field soils the lime content should be about one to three times greater than that of magnesium.

Hopkins,³ in 1910, reported the results of experiments carried on at Illinois by himself and associates wherein it was demonstrated by means of pot cultures that magnesium carbonate exerted a beneficial action upon the growth of cereals until the addition of the magnesium carbonate reached 0.8 of one per cent., after which a detrimental effect was produced until the addition reached two per cent., when the addition of magnesium carbonate was fatal to the growth of cereals. The addition of lime in the form of gypsum in the ratio as advocated by Löew (7 : 4) exerted no effect on the toxic action of the magnesium carbonate. Hopkins, therefore, concluded that Löew's ratio received no support from his investigations. He found, however, that the double decom-

In 1910, Löew¹ discussed some recent work regarding his advocated ratio of lime to magnesia of 1 : 1 and maintained that the work discussed did not refute the theory.

Hilgard,² with respect to magnesia in soils in excess, says: "Soils containing large proportions of magnesia generally are found to be unthrifty, the lands so constituted being frequently designated as 'barrens.'"

In view of this conflicting evidence regarding the validity of the lime-magnesia ratio, it is very interesting to study the results obtained from a natural soil formed from the disintegration of limestone, quartzite and dolomite with the formation of a soil containing over 40 per cent. of calcium-magnesium carbonate, of which nearly one-third is magnesium carbonate.

The Greenville Farm, one of the experimental farms belonging to the Utah Experiment Station, is in the Great Basin district. The soil of this farm was formed by the weathering of the near-by mountain range which consists largely of limestone, quartzite and dolomite. At the time of Old Lake Bonneville, the streams loaded with the decomposed rock particles of limestone, quartzite and dolomite met the quiet waters of the lake and deposited their load. It is of the finer particles thus deposited that the soil of this farm is composed.

In Table I are recorded the results obtained by the mechanical analysis of the soil. The degree of fineness of the particles may have some bearing on the results obtained on this farm.

TABLE I.—PHYSICAL ANALYSIS OF THE SOIL OF THE GREENVILLE FARM.

Depth in feet.	1.	2.	3.	4.	5.	6.	7.	8.
Coarse sand (above 0.5 mm.).....	0.21	0.17	0.68	1.02	0.09	0.34	0.47	0.09
Medium sand (0.1 to 0.32 mm.).....	9.63	8.29	6.63	9.63	9.53	9.48	8.91	7.08
Fine sand (0.032 to 0.1 mm.).....	30.04	32.54	9.49	33.06	36.92	33.79	35.34	34.25
Coarse silt (0.01 to 0.032 mm.).....	32.25	32.81	32.62	28.51	28.65	30.49	31.65	32.65
Medium silt (0.0032 to 0.01 mm.).....	12.30	10.46	10.89	10.95	10.46	10.85	9.92	9.89
Fine silt (0.001 to 0.0032 mm.).....	6.25	4.81	7.27	6.94	4.85	5.86	5.56	5.84
Clay (below 0.001 mm.).....	7.62	7.12	10.13	7.52	7.82	6.78	6.52	7.57
Moisture.....	1.60	1.47	1.13	1.49	0.95	1.01	1.01	0.84
Soluble and lost.....	0.10	2.33	1.16	0.83	0.73	1.40	1.42	1.99
Specific gravity.....	2.67	2.72	2.80	2.69	2.76	2.79	2.71	2.76
Apparent specific gravity.....	1.23	1.27	1.30	1.29	1.33	1.34	1.39	1.35
Water-soluble salts.....	0.06	0.11	0.14	0.16	0.08	0.09	0.15	0.09

The soil would be classified as a loam.

TABLE II.—CHEMICAL COMPOSITION OF THE SOIL OF THE GREENVILLE FARM.

Depth in feet.	1.	2.	3.	4.	5.	6.	7.	8.
Insoluble residue.....	42.18	36.51	32.16	41.65	28.72	29.64	31.14	30.75
Potash, K ₂ O.....	0.67	0.89	0.59	0.82	0.61	0.74	0.79	0.75
Soda, Na ₂ O.....	0.35	0.47	0.47	0.62	0.37	0.42	0.45	0.74
Lime, CaO.....	16.88	17.80	21.34	15.60	22.62	23.15	22.24	21.78
Magnesia, MgO.....	6.10	9.46	7.57	7.48	9.36	5.89	6.06	5.63
Oxide of iron, Fe ₂ O ₃	3.03	2.69	3.46	2.95	2.17	2.42	2.47	2.54
Alumina, Al ₂ O ₃	5.64	4.69	3.40	6.09	5.33	8.07	7.90	9.03
Phosphoric acid, P ₂ O ₅	0.41	0.29	0.34	0.19	0.12	0.06	0.07	0.11
Carbon dioxide, CO ₂	19.83	23.11	26.67	20.88	29.31	29.57	28.80	28.13
Volatile matter.....	5.60	3.38	3.93	4.23	0.91	0.95	...	0.24
Total.....	100.69	99.29	99.93	100.51	99.52	100.91	99.92	99.68
Humus.....	0.53	1.00	0.61	0.47	1.13	0.60	0.44	0.57
Nitrogen.....	0.139	0.117	0.080	0.175	0.072	0.070	0.062	0.066
Water at 95 degrees.....	1.60	1.47	1.13	1.49	0.95	1.01	1.01	0.84

position reaction between the gypsum and the magnesium carbonate was effective when the soil was leached so as to remove the soluble magnesium sulphate.

The results obtained from a chemical analysis³ of the soil of this farm are recorded in Table II.

The soil is fairly well supplied with phosphoric

¹ *Chemical Abstracts*, 3, 2991.

² *Ibid.*, 3, 1565.

³ Hopkins, "Soil Fertility and Permanent Agriculture" (1910), p. 171.

¹ *Chemical Abstracts*, 4, 3269.

² Hilgard, "Soils," 382.

³ *Bull.* 106, Utah Experiment Station.

acid, but is low in nitrogen and humus. But from the point of view of this discussion the high content of lime and magnesia is noteworthy.

The results obtained for magnesium carbonate and calcium carbonate calculated from the magnesium oxide and calcium oxide, together with the ratio of lime (CaO) to magnesia (MgO), are recorded in Table III:

TABLE III.—PERCENTAGE OF MAGNESIUM CARBONATE AND CALCIUM CARBONATE AND RATIO OF LIME TO MAGNESIA. RESULTS EXPRESSED AS PER CENT. OF DRY SOIL.

Depth in feet.	1.	2.	3.	4.	5.	6.	7.	8.
Calcium carbonate.....	30.22	31.86	38.20	27.93	40.49	41.44	39.84	38.99
Magnesium carbonate.....	12.75	19.76	15.82	15.63	19.56	12.31	12.66	11.77
Ratio of lime to magnesia.....	1 : 2.8	1 : 1.9	1 : 2.8	1 : 2.0	1 : 2.4	1 : 4.0	1 : 3.6	1 : 3.8

The results indicate that nearly 43 per cent. of the surface foot of soil is calcium and magnesium carbonate and that the amount increases with depth to the fifth foot, after which the magnesium carbonate content is practically the same as in the first foot, while the calcium carbonate also increases with depth to a maximum in the fifth foot and then remains practically constant.

In Table IV are recorded the results obtained by calculating the amount of calcium-magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$) from the carbon dioxide as determined and also the combined carbonate as determined from the calcium and magnesium oxides.

TABLE IV.—PERCENTAGE OF CALCIUM-MAGNESIUM CARBONATE AS CALCULATED FROM CARBON DIOXIDE AND FROM LIME AND MAGNESIA. RESULTS ARE EXPRESSED AS PER CENT. OF DRY SOIL.

Depth in feet.	1.	2.	3.	4.	5.	6.	7.	8.
By calculation from CO_2	41.54	48.42	55.86	43.74	61.40	61.92	60.34	58.94
By addition of MgCO_3 and CaCO_3	42.97	51.62	54.02	43.66	60.05	50.75	52.50	40.76

The results indicate quite fully that to a depth of five feet the calcium and magnesium are nearly in the proportion that they occur in dolomite.

From the work as reviewed above one would almost conclude that such a soil would be sterile, but just the contrary is true; the soil is remarkably fertile and produces excellent crops even without the addition of barnyard manure.

In Table V are recorded the eight-year average results obtained by the application of an ordinary amount of irrigation water. The sugar beets were grown on the Frankhauser farm, which is separated from the Greenville farm by a road four rods in width. The soil of the former is similar to the latter, but the farms differ in that the former has received heavy applications of barnyard manure, while the Greenville farm has not. Sugar beets on this soil will not produce a profitable crop without the addition of barnyard manure.

TABLE V.—EIGHT-YEAR AVERAGE YIELD OF OATS, WHEAT, POTATOES AND SUGAR BEETS ON THE GREENVILLE FARM.

Crop.	Amount of water applied.	Treatment.	Average yield.
Oats.....	15"	Unmanured	82.0 bushels
Wheat.....	15"	Unmanured	50.4 bushels
Potatoes.....	20"	Unmanured	262.3 bushels
Sugar beets.....	15"	Manured	21.8 tons

This land has been cropped for nearly forty years and the Greenville farm, so far as we know, has never had any manure applied. The results obtained from

this soil show quite clearly that the high percentage of magnesia has no toxic action on the growth of the plants. It is evident that the magnesia does not have any toxic action on plant growth for one of two reasons: first, the ratio of magnesia to lime, which falls within the ratio (1 : 3), as recently suggested by Löew,¹ is favorable to plant growth, or, secondly, the calcium and magnesium are present in the form

of a double salt such as $\text{CaMg}(\text{CO}_3)_2$, and therefore magnesium carbonate, as such, exists in this soil only in small amounts. It seems possible that such a double salt would have a different action on plant growth than would either the magnesium carbonate or calcium carbonate alone.

Whatever may be the true explanation, the results reported here may have great practical value since they indicate that finely ground magnesian limestone may possibly be used on acid soils to correct the acidity in those sections of the country where such is necessary. The addition of limestone by artificial means for this purpose certainly would never reach

the amount actually present in this soil. Of course, the reaction which would take place between the added limestone and the many acids of the soil may give rise to the formation of new magnesium compounds which would prove to be toxic. This is a phase of the question which would have to be considered in the use of such limestone.

CHEMICAL LABORATORY,
UTAH EXPERIMENT STATION,
January 16, 1911.

THE CHEMISTRY OF ANAESTHETICS, I.: ETHYL ETHER.²

(Concluded from May issue.)

By CHARLES BASKERVILLE AND W. A. HAMOR.

IV. THE CHANGES WHICH OCCUR IN ETHYL ETHER DURING STORAGE.

Schönbein³ studied the action of oxygen and air on ether in the light, and found that it becomes oxidized, responding to the tests for ozone. This investigation was the first conducted with the view of ascertaining the nature of the oxidation of ether, and led to the later assumption that ozone is produced by the action of air and light on ether, and that it may exist in ether in solution.⁴ That such a view is untenable and is not

¹ Löew, *Chemical Abstracts*, **3**, 1565 (1909).

² Read before the New York Section, American Chemical Society.

³ *J. prakt. Chem.*, **52**, 132, 183; *J. Pharm.*, [3] **20**, 258; *Arch. phys. nat.*, **17**, 61; see also, *Arch. Pharm.*, [2] **67**, 257. Gay-Lussac (*Ann. chim. phys.*, **11**, **2**, 98) had observed in 1816 the formation of an explosive, strongly oxidizing "oil" in ethyl ether.

⁴ For example, see Büchner, *Ber.*, **1885**, 376.

supported by facts now known, we shall endeavor to demonstrate by a consideration of the oxidation of ether under all conditions.

I. THE ACTION OF OZONE ON ETHER.

According to Houzeau,¹ ether exposed to the action of ozone is more rapidly oxidized than alcohol under the same conditions; hydrogen dioxide is produced. Wright,² however, found that dry ozonized oxygen acts with some violence on ether, forming acetic acid, oxalic acid, hydrogen dioxide, and a little formic acid. It is important to note that both found hydrogen dioxide among the products of oxidation; that is, a substance occurred in the ozonized ether which responded to the tests for this substance, which fact is in harmony with the later observations of Berthelot,³ who found that sirupy ethyl peroxide is formed when ethyl ether is ozonized.

Nef⁴ has shown that ethyl peroxide consists mainly of acetic peroxide ($C_4H_6O_4$), which was first obtained by Brodie.⁵ This peroxide owes its oxidizing and explosive character to its ready dissociability into ozone and acetic anhydride; in fact, if kept in loosely closed vessels, it is completely converted into acetic anhydride and acetic acid at the end of four months.

Clover and Richmond⁶ found that the aqueous solution of acetic peroxide gradually suffers hydrolysis with the formation of molecular proportions of acetic and peracetic acids, and that the latter slowly changes into acetic acid and hydrogen dioxide. Later, Clover and Houghton⁷ showed that acetic peroxide is produced by the action of peracetic acid on acetic anhydride, and that when acetic peroxide is dissolved in an aqueous solution of hydrogen dioxide, peracetic acid is produced. These facts would seem to demonstrate what while Wright did not conduct the process of ozonization to the limit, Berthelot obtained a more or less pure acetic peroxide by the direct action of ozone.

The substance prepared by Harries⁸ by passing ozone and carbon dioxide into "dry ether," contained 15.28 to 25.65 per cent. of carbon as against the 58.54 per cent. required for ethyl peroxide,⁹ and was undoubtedly an impure acetic peroxide, which contains 40.67 per cent. of carbon.

A consideration of the action of ozone on various carbon compounds will throw light upon the problem.

Schönbein¹⁰ found that turpentine became oxidized quite readily and than an active substance was thus formed; and Soret¹¹ found reasons to believe that ozone is completely absorbed by turpentine and oil of cinnamon. Kingzett¹² supplied data to confirm this, for he learned that ozonized turpentine contains peroxidized compounds which react with water.

¹ *Compt. rend.*, **75**, 142.

² *Am. J. Sci.*, [3] **7**, 184.

³ *Bull. soc. chim.*, [2] **36**, 72.

⁴ *Ann.*, **298**, 202.

⁵ *Proc. Roy. Soc.*, **9**, 363.

⁶ *Am. Chem. J.*, **29**, 179.

⁷ *Ibid.*, **32**, 43.

⁸ *Ann.*, **343**, 311.

⁹ Assuming the formula to be $(C_2H_5)_4O_3$.

¹⁰ *Loc. cit.*

¹¹ *Ann. chim. phys.*, [4] **7**, 113.

¹² *J. Chem. Soc.*, **37**, 800.

It would appear to be demonstrated that in general ozone acts on carbon compounds in two ways: (1) to form an ozonide, when the ozone attaches itself to an unsaturated carbon linking; and (2) when the ozone molecule is decomposed, labile peroxides of the carbonyl group being formed. These facts are mainly due to the elaborate series of investigations conducted by Harries, who has shown that mesityl oxide yields a peroxide when ozone is passed into it;¹ that aliphatic aldehydes in general are not attacked by ozonized oxygen;² and that methyl alcohol is oxidized by ozone to formaldehyde.³ According to Harries⁴ the nature of the reaction between ozone and unsaturated compounds depends on the presence or absence of water. In the absence of a solvent or in non-dissociating solvents, ozone is added at the double linking, forming ozonides. In the presence of water, these ozonides are decomposed forming ketones or aldehydes and hydrogen dioxide. It is possible that a small quantity of water may be sufficient to cause this decomposition, probably through catalytic action. The ozonides are mostly highly explosive, and in addition to the ones mentioned above, the following have been prepared: ozonides of allyl alcohol, secondary methylheptenol, tertiary dimethylheptenol, allylacetone, citronellal, citral, isocrotonic acid, oleic acid and elaidic acid, and mesitylenetriozone.

In conclusion, it would seem to be established that "dry ether" is acted upon by ozone with the production of an active, explosive substance, consisting mainly of acetic peroxide, and that this is produced by the decomposition of the ozone molecule. In the case of moist ether, the changes which result would be analogous to those which occur during the slow combustion of ether when exposed to the action of atmospheric oxygen in the presence of water, and these will now be referred to.

II. THE ACTION OF OXYGEN ON ETHER.

Evidence indicates that a peroxide may be formed in ether by the union of molecular oxygen with ethyl oxide in the slow process of "autoxidation." The employment of ether which had been carelessly stored has often resulted in unexpected phenomena, which have been found to be due to a substance resembling hydrogen dioxide, but one of much greater activity and of an explosive character.

Cleve⁵ concluded that the explosive nature of a substance formed from ether was due to ethyl peroxide; König⁶ found that explosive results in ether residues were due to the presence of a substance responding to the tests for hydrogen dioxide; Schär reported that ether which contained an extremely high percentage of "hydrogen peroxide" (over 5 per cent.) violently decomposed during an evaporation in a fat estimation, the explosion being favored by the presence of acetic

¹ *Ber.*, **36**, 1933; cf. Vanino and Thiele. *Ber.*, **29**, 1724.

² *Ibid.*, **36**, 2996. It will be shown later, however, that acetaldehyde gives a peroxide on slow oxidation, according to several investigators.

³ *Ibid.*, **36**, 3658; cf. Renard, *Ann. chim. phys.*, [5] **16**, 289.

⁴ *Ibid.*, **37**, 839; see also *Ann.*, **343**, 311.

⁵ *Chem. News*, **63**, 101.

⁶ *Mon. Sci.*, [4] **4**, 2. *Landwirtschaftl. Versuchsstat.*, **37**, 1.

and formic acids;¹ von Neander² drew attention to certain instances in which the residues left after the evaporation of ethereal extracts exploded, concluding that these explosions were apparently due to the active oxygen; and Kleemann³ and Hertkorn⁴ reported similar experiences. In view of all these communications it is only to be concluded that ether may contain a peroxide, formed, no doubt, when it is carelessly stored.⁵

Rossolimo⁶ found that a perfectly pure ether showed a strong oxidizing power after it had remained in a wash-bottle exposed to the action of the air for about three months, during which time evaporation had been proceeding slowly; and he learned that the oxidizing action of the peroxide contained in ether thus oxidized is a much greater one than that of hydrogen dioxide.⁷ Ditz⁸ has also found that peroxides, when present in ether, are more active than aqueous hydrogen dioxide; and we have observed this on several different occasions. This "activity" is undoubtedly due to the presence of a peroxide other than hydrogen dioxide, since an "inactive" ether can be rendered "active" by conducting through it a current of ozonized oxygen and then leaving it at rest some months;⁹ and although such a peroxide responds to all tests for the detection of hydrogen dioxide, and the latter is also a likely impurity as well, especially when the ether has been oxidized in the presence of moisture, it would appear to be well demonstrated that ether is capable of peroxidation.¹⁰

That a peroxide or peroxides exist in "active" ether may be inductively demonstrated by a consideration of the methods to which it is necessary to resort in order to eliminate the "activity." It has been shown by Dunstan and Dymond¹¹ that ether may be purified from peroxides by the use of an ample quantity of lime, and then twice washing with alkaline water;¹² but the following methods lend particular support to the matter under consideration:

1. Garbarini¹³ made experiments with a view of removing the oxidation product contained in ether that has been exposed to air, and found that a dry

¹ Arch. Pharm., **25**, 632.

² Chem.-Ztg., **26**, 336.

³ Ibid., **26**, 385.

⁴ Ibid., **26**, 407.

⁵ In this connection, see Thoms, Pharm.-Ztg., **1894**, 777; Ber. Pharm. Ges., **1894**, 10, 11. See also, Kappers, Dissertation Groningen, **1871**; and Walton, Am. Druggist, Aug. 8 (1910), p. 69.

⁶ Ber., **38**, 774.

⁷ An analogous case is found in the case of oleic acid. Harries and Thieme (Ber., **39**, 2844) have found that "oleic acid ozonide peroxide" gives a much more intense hydrogen dioxide reaction than the normal ozonide, when boiled with water.

⁸ Chem.-Ztg., **25**, 109; Ber., **38**, 1409.

⁹ Matignon, Compt. rend., **138**, 82.

¹⁰ Brühl (Ber., **28**, 2847) found that on one occasion when hydrogen dioxide was isolated by the help of ether, the specimen smelled strongly of ozone and an oily substance remained which possessed explosive properties. He did not consider that this substance could be acetic peroxide, however (Ber., **33**, 1709); cf. Stähler, Ber., **38**, 2619.

¹¹ J. Chem. Soc., **57**, 584.

¹² An ether so treated 10 years old showed no trace of peroxides. This, along with facts to be mentioned hereafter, shows the fallacy of the statement that ozone, formed by the decomposition which occurs under the influence of light and heat at the time the test for peroxides is applied, is the cause of the peroxide response.

¹³ Bull. Assn. Chim. Sucr. et Dist., **26**, 1165. Ferrous sulphate solution is also suitable (Stokes and Cain, J. Am. Chem. Soc., **29**, 410).

preparation of ferrous hydroxide is a suitable reagent for the purpose.

2. Ramsay¹ stated that the effects due to the presence of peroxides may be obviated by putting some clean mercury in the ether container, whereby the peroxides are decomposed.²

3. Ditz³ found that ether purified by Brunner's method by agitating with powdered potassium permanganate still contained a substance or substances which are similar to peroxides; but that ether treated with solid caustic potash according to Börrigter's method was freed from peroxides.

Ether may also be freed from peroxides by treatment with manganese dioxide,⁴ with chromic acid, or by treatment with sodium, potassium-sodium alloy, phosphoric anhydride, or a solution of sulphurous acid and hydriodic acid.

Considering that sufficient data have been given to justify the statement that we may assume the existence of peroxidized substances in "active" ether on *a priori* grounds; we shall now refer to the changes *in toto* which occur in ether during its autoxidation.

Regnault found that ether, after standing, no longer has a constant boiling point; and Ramsay and Young⁵ found that such ether acts on mercury, but that after agitation with mercury and distilling it does so no longer. However, up to 1876, ordinary ethyl ether had been credited with the power of producing ozone, and, beyond this, the subject was in a similar state to that which occurred in the case of the so-called formation of ozone by the oxidation of the essential oils. That is to say, nothing was known about it, beyond that under these conditions there had been recognized a substance which was mistaken for ozone, and of whose production there was no logical explanation. In 1876, Kingzett⁶ found that ethyl ether gives, apparently by atmospheric oxidation, "acetic ether" and hydrogen dioxide. He concluded that the changes which occur may be explained as follows: First, the ether is oxidized into "acetic ether" and water; second, the ester is oxidized into the anhydride, and that into acetic peroxide; and finally, the latter is decomposed with water, simultaneously with its formation. From Kingzett's experiments, it appeared that ordinary atmospheric oxygen plays the same part as the oxygen of the barium peroxide in Brodie's method of preparing acetic peroxide; that is, he considered that the reaction which occurs is similar to that which we know takes place when ether is ozonized.

Shortly afterwards, Legler⁷ found that when ether is oxidized by a red-hot platinum spiral, it gives formic

¹ Nineteenth Century, April, 1898.

² We have found that finely divided mercury is very suitable for removing peroxides occurring in ether.

³ Chem.-Ztg., **25**, 109.

⁴ Rep. Chem.-Ztg., **1889**, 46.

⁵ Chem. News, **61**, 237. Linebarger (Ibid., **70**, 53) observed that mercury on being brought into contact with certain ether of German manufacture, such as he employed in the determination of the boiling point, tarnished, and that the impurity thus removed exercised a considerable influence on the boiling point. In one case the boiling point was diminished 0.9° C.

⁶ Ibid., **34**, 136.

⁷ Ann., **217**, 381.

acid, acetic acid, aldehyde, acetal,¹ formaldehyde, and trimetric prisms of $C_{11}H_{22}O_{11}$. These prisms were found to be soluble in water, alcohol, and ether, and were decomposed by alkalis into formaldehyde and formic acid. The compound liberated iodine from potassium iodide solution and reduced lead dioxide, therefore appearing to be a derivative of hydrogen dioxide.

The investigation of the production of hydrogen dioxide in ether under such conditions as might obtain during storage was initiated by the investigations of Richardson. He found² that hydrogen dioxide is formed when water containing pure ether is exposed to light in an atmosphere of oxygen; and from an extended series of experiments, he observed the following: (1) the amount of hydrogen dioxide formed depends on the proportion of ether to water present; (2) no hydrogen dioxide is formed when a mixture of water-vapor ether-vapor, and oxygen is exposed to sunlight; (3) no hydrogen dioxide is formed when water and ether are exposed in an atmosphere of carbon dioxide; (4) no iodine is liberated from potassium iodide by a mixture of water, ether, and oxygen, from which light has been excluded.

From these and other experiments, he was led to believe that the oxidation under the influence of light involves initially an oxidation of water to hydrogen dioxide, and that oxidation of ether is a result of a secondary interaction between it and the hydrogen dioxide produced.

In partial contradiction to the findings of Richardson, Dunstan and Dymond³ found that pure ether, either wet or dry, does not form hydrogen dioxide when exposed to light, that ether prepared from methylated spirit yields hydrogen dioxide when kept for some time, but not if it has been previously purified by means of dilute chromic acid; that hydrogen dioxide is formed when ozone acts on ether in the presence of water; and that hydrogen dioxide is produced when certain conditions are maintained during the slow combustion of ether in contact with water, *i. e.*, pure ether may yield hydrogen dioxide when imperfectly oxidized, that is to say, hydrogen dioxide is formed as an intermediate product in the process of oxidation of ethyl ether.

Richardson⁴ then repeated the work of Dunstan and Dymond, and found that hydrogen dioxide is formed in ether in every case after exposure to light in contact with moist air or oxygen, but not in the dark at the ordinary temperature. He learned that ether and moist oxygen, exposed to a temperature of 75° to 88° C. in the dark, contained, after four days, considerable quantities of hydrogen dioxide; and similar results were obtained when ether and oxygen were kept at 60° C. for forty hours. Hence, it appeared that when special precautions are taken to ensure the presence of oxygen over ether, hydrogen dioxide is formed at the ordinary temperature, and even at 0° in the light, but not in the dark; it was found, however, that it is formed in the dark at about 60° C.

In his first paper, Richardson attempted to prove that when hydrogen dioxide is formed from moist ether, the water and not the ether is oxidized. Dunstan and Dymond opposed this view, as they considered that they were in possession of evidence that the ether itself is oxidized; and in his later contribution, Richardson appeared to abandon his former view, although he still contended that hydrogen dioxide could be formed from water and oxygen alone in the presence of light.

In the experiments made by Dunstan and Dymond, it was always observed that when hydrogen dioxide is produced in ether, the latter afterwards contains aldehyde, acetic acid, and other substances. Richardson also found that other products of decomposition are formed when ether is exposed to light. In fact, he and Fortey¹ later found that "dry ether" gives a well marked peroxide reaction after three days' exposure to "dry oxygen;" and that when ether is exposed for many weeks in the presence of oxygen and water it becomes rich in hydrogen dioxide and gives an acid reaction. They also proved that aldehyde is formed, and regarded it as the intermediate product. Similar results were obtained by Berthelot,² who found that ether, when mixed with water and exposed to air and sunlight for five months, yields aldehyde, alcohol, acetic acid, and methane; and with hydrogen dioxide, air and water, much larger yields of the same substances resulted. In direct accord with these results is the recognition of the fact that when ether is stored in badly stoppered bottles in the light, it forms considerable amounts of peroxides and other oxidation products, especially acetaldehyde.³

Since aldehydes can hold ozone in solution for a comparatively long time without becoming oxidized, it is exceedingly likely that they form peroxides with it, possibly analogous to the compounds they form with sodium hydrogen sulphite; and as acetaldehyde is only oxidized slowly by air to acetic acid, it is probable that it is peroxidized during the slow oxidation of ether. Ludwig⁴ has found that all the known aldehydes possess the power of absorbing and retaining oxygen in an active or ozonized condition, in which state they are able to liberate iodine, even from very dilute solutions of potassium iodide (1 : 600,000). Since ozonized acetaldehyde may be prepared by exposing acetaldehyde merely to the air, it could be formed under the conditions which obtain in badly stored ether, and its high "activity," and from the fact that it gradually becomes inert in the presence of water, would serve to explain phenomena observed in the case of oxidized ether.

Since Lieben and Berthelot have shown that alcohol is formed during the alteration of ether, and owing to the common occurrence of alcohol in ether, it is appropriate in this connection to consider what changes it undergoes during the oxidation of ether in which it

¹ *Proc. Chem. Soc.*, **1896**, 165.

² *Compt. rend.*, **129**, 627.

³ In this connection, see Thoms, *Pharm.-Ztg.*, **1894**, 777; also Poleck and Thümmel, *Arch. Pharm.*, [3] **27**, 961.

⁴ *Ber.*, **29**, 1454. According to Baeh (*Compt. rend.*, **124**, 951), acetaldehyde gives a peroxide on slow oxidation in the air, either in the light or dark. "On the Oxidation of Aldehyde," see Slaboszewicz, *Z. physik. Chem.*, **42**, 343.

¹ The probable occurrence of acetal in ether will be referred to later.

² *Chem. News*, **60**, 255.

³ *Ibid.*, **61**, 237; *J. Chem. Soc.*, **57**, 584.

⁴ *Chem. News*, **62**, 256.

is contained. Mathieu¹ has found that alcohol in wine-strength is converted into aldehyde by simple contact with the air at the ordinary temperature, and that the action is markedly accelerated by the presence of oxidizable bodies in the solution and by exposure to sunlight. In direct confirmation of this, assuming, of course, that aldehyde is the intermediate product of such oxidation, we have the results of Duchemin and Dourlen,² who have determined that alcohol is gradually oxidized in contact with air with the production of acetic acid.

It is therefore entirely reasonable to suppose that alcohol occurring in ether or that formed during its oxidation is also subject to oxidation of the following order: alcohol, aldehyde (aldehyde peroxide), acetic acid. In such a conversion, the degree of acidity is liable to vary more or less in both directions in short intervals during storage in glass vessels, just as in the case of the oxidation of ether itself. The variations in acidity—theoretical, but not sensible in general—may be due to differences between the rapidity of the oxidation and the saturation of the acids by the bases of the glass. In fact, it should be mentioned here that the nature of the ether container is of vast importance in the light of the oxidation changes which are possible. The extent of the oxidation—or, for that matter, any oxidation at all—is dependent upon the quality of the glass used in bottles for storing ether; and in the case of metallic containers, in view of some recent researches, it is probable that all metals which show anomalous anodic conductivity are likely to develop free hydrogen dioxide in contact with water and oxygen.³ The presence of such metals should, therefore, be guarded against.

III. THE COMBUSTION OF ETHER.

When a mixture of ether vapor and air comes in contact with platinum black, heated platinum-sponge, or other bodies heated not quite to redness, it undergoes slow and imperfect combustion, forming aldehyde, acetic and formic acids, carbon dioxide, water, etc.; and when ether vapor is passed through a red-hot tube, ethylene, water, carbon monoxide, and aldehyde are produced. Of especial interest, however, is the fact that just as burning hydrogen produces hydrogen dioxide, so does the flame of ether.⁴

IV. SUMMARY.

The conclusion from the preceding is that the oxidation of commercial ether in the presence of moisture would appear to be productive of a series of complex conversions, initiated, however, by the formation of hydrogen dioxide. The slow combustion of pure ether in the presence of water, and under such conditions as exist when it is improperly stored, would appear to occur in the following stages:

¹ *Bull. Assn. Chim. Sucr. Dist.*, **22**, 1283.

² *Compt. rend.*, **140**, 1466.

³ Barnes and Shearer, *J. Phys. Chem.*, **12**, 155, 468. Ordinary distilled water sometimes shows distinct properties of an indirect oxidase, and Tixier (*Bull. Sci. Pharm.*, **1910**, 17; *Pharm. J.*, **84**, 645) attributes such oxidizing properties to extremely minute traces of copper derived from the distilling plant. It is likely, however, that these properties are due to the presence of small amounts of hydrogen dioxide developed by copper in contact with water and atmospheric oxygen.

⁴ Engler, *Ber.*, **33**, 1109.

1. The formation of hydrogen dioxide from water and oxygen of the air. This is particularly likely in cases where there is direct exposure to light, and it is more or less activated by contact action.

2. Dissociation of hydrogen dioxide into water and oxygen, which latter then exerts a direct oxidizing action, resulting in the formation of the following: acetic peroxide, acetaldehyde and acetaldehyde peroxide, and eventually acetic acid. The formation of acetic peroxide facilitates a series of oxidations, and by its hydrolysis alone, acetic and peracetic acids are formed. The peracetic acid would then become converted into acetic acid and hydrogen dioxide. Therefore, it is reasonable to conclude that a continuous cycle of changes occurs in ether during its oxidation, and that such changes result in the simultaneous formation and occurrence of peroxidized compounds, intermediate (aldehyde) and ultimate (acetic acid) resultants.

When anhydrous ether is exposed to the action of atmospheric oxygen during improper storage, there is every reason for the conclusion that peroxidation occurs. Such action is similar to that which takes place when anhydrous ether is ozonized, but the process is much less active, being indirect. During storage under conditions which would be conducive to oxidation, the absolute exclusion of moisture is not attained. It is, therefore, to be concluded that changes occur similar to those which ensue in the presence of water, but of a much slower and much less intense nature.¹

In confirmation of the views expressed above on the formation of peroxides in ether during careless and improper storage, the authors are able to furnish experimental proofs which would seem to establish beyond any doubt the fact that ether of anaesthetic grade contains peroxidized compounds after exposure to varying temperature conditions and sunlight, in the presence of atmospheric oxygen, for considerable periods of time, especially when it is stored in colorless glass vessels or in badly stoppered tin containers.

"Ether was allowed to stand for 200 days in 150 cc. tin containers, partly filled, stoppered as well as the mouth of the containers would permit, and exposed to varying temperature conditions inside of a window with southern exposure. The conditions of storage were similar to those which obtain in many laboratories and hospitals. It should be mentioned that none of the samples so exposed exhibited a peroxide reaction originally, but all contained small amounts of water and alcohol. The following results were obtained, using the vanadic acid and cadmium potassium iodide tests:

"No. 1A (container one-fifth full): strong peroxide reaction; strongly acid.

"No. 1B (container one-half full): marked peroxide reaction, but less pronounced than in No. 1A; strongly acid.

¹ Although it may appear from evidence that ether is subject to direct peroxidation, hydrogen dioxide being formed from the acetic peroxide by a secondary process—by the action of water, yet the precautions taken to exclude water have not been such as to assume that direct peroxidation occurs and it is likely that the presence of water is necessary (cf. Armstrong, *J. Soc. Chem. Ind.*, **24**, 479).

"No. 1C (container four-fifths full): very faint peroxide reaction.

"No. 2A (container two-thirds full): no peroxides present. This container was provided with a tightly fitting stopper. The neck of the can was cylindrical, whereas those holding the preceding were provided with a conical neck, and it was thus possible to cork the can more securely.

"No. 2B (one-half full): no peroxides present. This sample was stoppered similarly to No. 2A.

"No. 3A (one-tenth full): strong peroxide reaction.

"No. 3B (one-third full): no peroxides present. This container was properly stoppered.

"No. 3C (three-fourths full): no peroxides present. Container was well stoppered.

"No. 3D (four-fifths full): no peroxides present. Container was properly stoppered.

"The various fractions from three samples of ether were exposed to varying temperature conditions for 193 days. These fractions were contained in 20 cc. tube vials (colorless glass) and in every case were well stoppered. None had contained peroxides originally. The following results were obtained:"

Fractions.	A.	B.	C.
34—36°	Container half full. Pronounced peroxide reaction. Acid reaction.	Four-fifths full. Faint, yet decided reaction.	One-third full. Traces of peroxides.
36—39°	One-fifth full. Marked reaction; acid reaction strong.	Two-thirds full. Traces of peroxides.	One-half full. Traces of peroxides.
39—42°	One-fifth full. Marked reaction.	One-third full. Traces of peroxides.	Two-thirds full. Traces of peroxides.

In order to determine whether peroxides are formed in anhydrous ether¹ when it is exposed to light and varying temperatures, ether distilled over sodium was subjected to extreme conditions for two weeks in various containers. The results obtained may be tabulated as follows:

Description of container.	Results after 2 weeks' exposure to light and extreme temperature conditions.
500 cc. glass stoppered ether bottle, containing 250 cc. of anhydrous ether (only impurity originally, traces of acetaldehyde). During the exposure, the ether had slowly evaporated, and at the time of the test the bottle contained but 50 cc.	Strong peroxide reaction.
150 cc. tin container, well stoppered with a cork. This container was originally one-half full and no evaporation had occurred at the end of two weeks, apparently.	No peroxides present.
50 cc. glass tube vial, poorly stoppered. The vial originally contained 25 cc. but considerable evaporation occurred during the exposure.	Strong peroxide reaction.
Glass-stoppered Erlenmeyer flask of 50 cc. capacity. This flask had contained 25cc. of ether, but considerable evaporation had occurred.	Decided peroxide reaction.

From these experiments, it is concluded that peroxides, or peroxidized compounds, may form in ether of all grades which is improperly stored, and that such impurities are most likely to be generated by exposing partially filled containers to varying atmospheric conditions, for continued periods of time. The extent of the oxidation of both pure and anaesthetic ether is dependent upon the nature of the container, the purity of the sample, the amount of air present, and, in glass vessels, the intensity of the light, which accelerates the oxidation. Ether should not be stored in glass vessels for any length of time without being tested for oxidation products before use;

¹ One sample of "concentrated" ether which we obtained from a well known firm was found to be rich in peroxidized compounds. This sample, which had been imported from Germany in a can, was contained in a brown glass bottle, into which it had been emptied after the can became corroded. The bottle was entirely filled and well-stoppered; the oxidation must, therefore, have occurred while the ether was in the defective tin container.

and the tin containers should be of such capacity that they need not be opened before being emptied when the ether is employed for anaesthetic purposes. In laboratories, ether should always be kept in completely filled, well-stoppered dry glass bottles, preferably those made of non-soluble blue, green or brown glass, excluded from the light, in cool, dry places, and over mercury, or preferably sodium. If the container is cork-stoppered, the bottom of the cork should be completely covered with tin-foil to prevent penetration of the stopper, with consequent shrinkage and leakage, and to prevent the extraction of organic matter.

V. ON THE EXISTENCE OF ETHENOL IN ETHYL ETHER.

A few compounds of the type of vinyl alcohol are known. In many cases in which their formation might be expected, their isomers are obtained; for example, when water is abstracted from glycol, $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$, vinyl alcohol, CHOH , does not result, but an isomer,



acetaldehyde, CH_3 ; and vinyl alcohol has never



been prepared in a pure condition. However, Poleck and Thümmel² suppose that vinyl alcohol, or ethenol ($\text{CH}_2 : \text{CH.OH}$), is present in ether that has been exposed to air and sunlight, and that its presence is indicated by the formation of a precipitate ($\text{C}_2\text{H}_5\text{O}.\text{HgO}.\text{Hg}_2\text{Cl}_2$) when a solution of mercury oxychloride

in sodium carbonate is added to common ether.³ This precipitate, according to them, is white and is converted by boiling potash into explosive greenish black "acetylene mercury" ($\text{C}_2\text{H}_2\text{O}_4.\text{Hg}_4$), and by adding nitric acid to its alkaline solution into $\text{C}_2\text{HHg}_2\text{OCl}_2$, which is not explosive.

With regard to the formation of ethenol which they found in commercial ethers, Poleck and Thümmel consider that it is formed partially during the preparation of ether and partly by the action of atmospheric oxygen with the simultaneous formation of hydrogen dioxide, which reacts on ether with the production o

¹ Ber., 22, 2863; see Arch. Pharm., [3] 27, 961.

² This is founded on an observation by Thümmel (vide Am. J. Pharm., 62, 15). In an examination of the oxychlorides of mercury, he attempted to remove an excess of mercuric chloride from a solution of monoxochloride of mercury in sodium dicarbonate, by agitation with ether; but this was found to be impossible, as the ethereal solution after some minutes became turbid and deposited a white precipitate, which was found to be due to the presence of "vinyl alcohol."

a further quantity of vinyl alcohol. They found that it may be removed by repeatedly shaking ether with water or by treatment with bromine, phenylhydrazine, or potassium hydroxide.

Since the publication of the above results, it has been quite generally assumed that ether forms vinyl compounds during storage,¹ and in several instances, attempts have been made to explain unusual reactions by attributing these to the presence of ethenol in the ether used. For example, Rimini² found that after shaking cheese with concentrated hydrochloric acid to dissolve the casein, gentle heating and shaking with ether in some cases produced an azure-violet coloration, the intensity of which varied with the sample of ether used. Pure ether, recently distilled over lime and sodium, gave no color, and Rimini stated that the formation of the color was due to the presence of vinyl alcohol in the ether used. Matignon also found reasons to definitely assert that vinyl alcohol occurs in some commercial ethers. He reported³ that commercial ethers which contain vinyl alcohol afford a sensitive reagent for vanadic acid, since they give a rose coloration with solutions of ammonium vanadate or vanadic acid containing 0.1 mg. of vanadium pentoxide per liter. He stated that when the ether is allowed to evaporate spontaneously, the residue becomes richer in vinyl alcohol and gives the characteristic rose color with solutions containing 0.02 mg. per liter; and that the blue color afforded by using "active ether" and pyrogallol is more delicate than with the latter alone. That vinyl alcohol is the active principle in the ethers capable of giving the color reaction was "proved" by the following facts: (1) The active ethers gave a white precipitate with a solution of mercuric chloride and potassium hydrogen carbonate; (2) they lost their activity after treatment with potassium hydroxide, which "resinifies the vinyl alcohol;" (3) they became inactive after being shaken with water, which "dissolves the vinyl alcohol." Matignon found that an "inactive" ether can be rendered "active" by passing a current of ozonized oxygen through it, and then leaving it at rest some months; and stated that ferric salts and chromates also give colorations with "active" ether, and must be removed before testing for vanadates.

It would seem that reactions attributable to known oxidation products of ether (peroxides, acetaldehyde) have been incorrectly ascribed to the presence of ethenol in every case in which the occurrence of the latter has been reported. Vinyl alcohol may be formed in the oxidation of ether, but we shall endeavor to show that its existence in commercial ethers has never been conclusively demonstrated, and this with due regard to the painstaking work of Poleck and Thümmel.

The assumption of the presence of vinyl alcohol in commercial ethers is entirely based upon the deportment of such ethers with mercury oxychloride. In such cases, white amorphous vinyl mercury oxychloride is precipitated, and this, on treatment with potas-

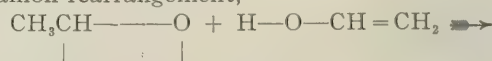
sium hydroxide, is converted into a black explosive powder, and on treatment with a haloid acid yields vinyl compounds; but, as a matter of fact, no definite proof is thus given of the existence of vinyl alcohol or vinyl compounds in an ether which positively responds to the test with mercury oxychloride, and the reaction is undoubtedly due to the presence of a known and long-recognized impurity of commercial ethers, namely, acetaldehyde, vinyl alcohol molecules forming from it during the progress of the reaction.

The compounds which acetaldehyde yields with various mercuric salts have received no little attention. Deniges⁴ found that acetaldehyde forms the compound $\text{SO}_4 : (\text{HgO})_2 : \text{Hg} \cdot \text{C}_2\text{H}_4\text{O}$ with mercuric sulphate; Lasserre⁵ obtained a compound, $\text{CH}_3\text{COH} \cdot \text{HgO}$, by the addition of sodium hydroxide to a solution of mercuric acetate and acetaldehyde; and Auld and Hantzsch⁶ found that the action of mercuric oxide on acetaldehyde in slightly alkaline solution leads to the formation of a colorless solution which probably contains trimercuri-di-aldehyde hydroxide, since it is quite indifferent towards phenylhydrazine, hydroxylamine, or rosaniline decolorized by sulphurous acid. They found that the substance could not be isolated, since it changes more easily than the acetone compound into the polymeride, $(\text{C}_4\text{H}_8\text{O}_5\text{Hg}_3)_x$, which is formed immediately as a white powder by warming a dilute solution of acetaldehyde with a solution of mercuric chloride made alkaline with potassium hydroxide. The formation of this polymeride is one of great significance in this connection, for it results on treating a dilute solution of acetaldehyde in ether with alkaline mercuric chloride. It is necessary, however, to show that vinyl alcohol molecules form under similar conditions; and, as will appear from what follows, this would seem to be established beyond question.

Michael and Kopp⁷ found that an aqueous solution of potassium carbonate gives aldol when allowed to act on aldehyde; and Nef⁸ and McLeod⁹ have proved that an aqueous solution of acetaldehyde contains vinyl alcohol molecules as soon as potassium or sodium hydroxide is present in amounts above 0.1 per cent. The vinyl alcohol, which is formed by intramolecular addition from the hydroxyethylidene,



is then at once absorbed by unchanged acetaldehyde, with anion rearrangement,



giving acetaldol, etc.

Denis⁷ showed that the correctness of the conclu-

¹ *Compt. rend.*, **128**, 429.

² This compound always contains a little mercurous sulphate, which fact is important, in view of the composition of the compound obtained by Poleck and Thümmel.

³ *J. Pharm. Chim.*, [6] **22**, 246.

⁴ *Ber.*, **38**, 2677.

⁵ *Am. Chem. J.*, **5**, 190.

⁶ *Ann.*, **298**, 316.

⁷ *Am. Chem. J.*, **38**, 565.

¹ For instance, see Thoms, *Pharm.-Ztg.*, **1894**, 777; *Ber. Pharm. Ges.*, **1894**, Parts 10 and 11; and Bertsch, *Apoth. und Drogist*, **1893**, No. 12.

² *Gazz. chim. ital.*, **29**, 1, 390.

³ *Compt. rend.*, **138**, 82.

sions of Nef and McLeod is thus established: When an aqueous solution of acetaldehyde is allowed to stand for a long time with freshly precipitated oxide of mercury, no action occurs in the cold; if, however, sodium hydroxide or carbonate is added, the aldehyde present is very rapidly and completely converted into white, insoluble, basic mercuric vinylate, $\text{Hg}(\text{OCH}=\text{CH}_2)_2 \cdot \text{HgO}$, from which, by the addition of dilute acids, acetaldehyde can again be regenerated quantitatively. This fully demonstrates that no vinyl alcohol molecules are present in an aqueous solution of acetaldehyde and that these appear only when sufficient alkali has been added. It also proves that vinyl compounds result from an acetaldehyde solution when reagents similar to those employed by Poleck and Thümmel are used.

Hofmann¹ found that when acetylene is passed through a solution of mercuric nitrate acidified with nitric acid, a fine colorless, crystalline precipitate results, which, after washing with 2 per cent. nitric acid solution and drying under reduced pressure, has the composition $\text{C}_2\text{Hg}_2\text{NO}_4\text{H}$. It is practically insoluble in water or 3 per cent. nitric acid, but is decomposed by concentrated acid. With warm, dilute hydrochloric acid, it yields acetaldehyde, and mercuric chloride goes into solution. When treated with alkalis, the nitrogen is obtained in the form of nitrates, and when warmed with sodium hydroxide and potassium cyanide solution, aldehyde resin is formed. Hofmann found that the compound may be obtained in the form of large crystals by using an alcoholic solution of aldehyde in place of acetylene; after remaining for fourteen days, large, colorless, doubly-refractive prisms were deposited. The constitution suggested was $\text{NO}_3 \cdot \text{Hg} \cdot \text{C}(\text{:Hg}) \cdot \text{CH} \cdot \text{O}$. Hofmann considered that the substance obtained by Poleck and Thümmel, by shaking commercial ether with an aqueous solution of mercuric chloride and potassium hydrogen carbonate, was probably a somewhat similar compound, only contaminated by a little mercurous chloride. This seems to be supported by experimental data, since the salts of the compound $\text{C}_2\text{Hg}_2\text{NO}_4\text{H}$ leave a gray residue consisting of mercury and the explosive oxymercarbide when treated with alkali.

Köthner,² commenting on the substance obtained by Hofmann by the action of acetylene on a solution of mercuric nitrate, mentioned that he had previously³ obtained results similar to those of Hofmann, and had drawn attention to the relationship of the substance to vinyl alcohol and acetaldehyde. Erdman and Köthner⁴ found that mercurio-carbide nitrate resembles Poleck and Thümmel's mercury derivative of vinyl alcohol, and that it yields acetaldehyde on treatment with dilute acids.

As has been intimated, our object is not to show definitely that vinyl alcohol does not exist in commercial ethers; but sufficient evidence has been given to show that acetaldehyde, an impurity of all commercial ethers, may be converted into a compound pos-

sessing the properties of the substance obtained by Poleck and Thümmel when an ether containing the substance in considerable amounts is agitated with mercury oxychloride.

We have found that the test usually specified for the detection of vinyl alcohol in ether is indicative of the presence of acetaldehyde, and therefore no reliance can be placed upon it as a test for vinyl alcohol.

The test given in the *Pharmacopée Française*¹ for vinyl alcohol was tried with samples of pure ether containing acetaldehyde. This is as follows:

50 cc. of the ether are shaken up with 4.5 cc. of a saturated solution of potassium hydrogen carbonate and 1 cc. of a saturated solution of mercuric chloride, after which no turbidity or white amorphous precipitate should result.²

This test is similar to the one proposed by Bertsch,³ who found that the presence of vinyl alcohol can be detected by shaking the ether under examination with mercury oxychloride. If, after ten or twenty minutes, a turbidity or a white amorphous precipitate results, which, on treatment with potassium hydroxide, is converted into a black explosive powder, the presence of vinyl alcohol may be assumed.

In the first test, the mixture of reagents possesses a pale yellow or reddish color from suspension of the oxychloride formed. At the beginning, the mixture is alkaline and the action results in the formation of a yellow oxychloride, but the alkalinity is overcome by the acid liberated, and a red oxychloride—probably tri-mercur-di-oxychloride—is formed. Carbon dioxide escapes and finally the liquid is alkaline, owing to the equilibrium condition of potassium chloride and mercuric oxide.⁴ It will therefore be observed that an alkaline solution is employed; and, as has been shown, when an acetaldehyde solution is thus treated, vinyl alcohol molecules will make their appearance under such conditions.

On adding 4.5 cc. of a saturated solution of potassium hydrogen carbonate and 1.0 cc. of a saturated solution of mercuric chloride to 50 cc. of an ether rich in acetaldehyde, but containing no other impurities, and shaking thoroughly, the reddish brown oxychloride changed to a white color on standing ten minutes, becoming pure white after fifteen minutes. A saturated solution of potassium hydrogen carbonate was then added to a saturated solution of mercuric chloride until the precipitate of oxychloride which first formed was dissolved to form a clear, reddish yellow solution. 5 cc. of this solution, on being well shaken with an ether containing about 1 per cent. of acetaldehyde, resulted in the formation of a white precipitate after five minutes' standing. Thus, the test specified by the *Pharmacopée Française* for the detection of vinyl alcohol is not indicative of the presence of that substance originally, and the vinyl compound which results, if

¹ 1908, 245.

² This test was proposed by Poleck and Thümmel (*Arch. Pharm.*, **227**, 964; *Z. anal. Chem.*, **29**, 717). They also placed the time limit of ten to twenty minutes.

³ *Loc. cit.*

⁴ Concerning the formation of mercury oxychloride in this reaction, see Millon, *Ann. chim. phys.*, [3] **18**, 372; Roucher, *Ibid.*, [3] **27**, 353; Thümmel, *Arch. Pharm.*, **227**, 589; and Schoch, *Am. Chem. J.*, **29**, 319.

¹ *Ber.*, **31**, 2212.

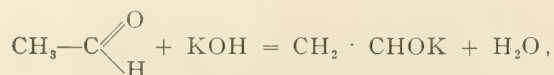
² *Ibid.*, **31**, 2475.

³ *Halle. a-S. Frühjahr*, 1896.

⁴ *Z. anorg. Chem.*, **18**, 48.

there be any, is unquestionably produced by the action of the reagents on acetaldehyde.

According to Poleck and Thümmel, the yellow or brown color imparted to commercial ether on the addition of potassium hydroxide is due to the presence of vinyl alcohol. We do not think so, since acetaldehyde is the cause of such coloration. In this case, too, a vinyl compound is probably formed, and as an intermediate product, by the action of potassium hydroxide on acetaldehyde. At all events vinyl alcohol molecules are present in the acetaldehyde solution so treated and, as in the reaction between sodium and acetaldehyde,¹ it is undoubtedly true that a vinyl alcohol compound, capable of only a brief existence, is formed, according to the following,



and that this soon decomposes, forming high molecular condensation products, as aldehyde-resin. It cannot be said, however, that the test with potassium hydroxide is indicative of the presence of vinyl alcohol.

With regard to the other communications dealing with the reported occurrence of vinyl alcohol in ether, it would seem that no efforts were made to establish the absence of acetaldehyde or peroxides in the samples of ether employed. The azure-violet color observed by Rimini may be explained in three ways: (1) that the hydrochloric acid used alone produced the color observed;² (2) that the peroxides occurring in the ether gave the coloration in the presence of aldehyde;³ (3) that the peroxides occurring in the ether gave the coloration in the presence of aldehydes from the cheese.

It is obvious that since the coloration may be satisfactorily accounted for by known reactions, it is unnecessary to attribute it to the presence of vinyl alcohol in the ether used.

With regard to the observations of Matignon, an ether containing peroxides and acetaldehyde, that is, an ether rendered "active" by ozonization, would deport itself similarly to the samples used by him. Treatment with potassium hydroxide would serve to remove both of these impurities; agitation with water would eliminate such "active" substances; and ether containing peroxides gives a rose color with vanadic acid.⁵

In conclusion, the occurrence of acetaldehyde in ether, especially in commercial ether, is well known, and this impurity fully accounts for the deportment of the ethers examined by Poleck and Thümmel. It would, therefore, seem, that any attempts to explain or establish the existence of ethenol in ether are un-

necessary with the data now at hand. Moreover, it has been shown that ethenol may be formed from the acetaldehyde produced from the oxidation of ether, or that present as a primal impurity, and that the reactions attributed to it may be accounted for in this manner.¹

VI. (a) ON THE DETECTION OF PEROXIDES IN ETHYL ETHER.

It has been shown that peroxidized compounds are produced through contact with air in the presence of light, as well as in the dark. The occurrence of these substances in anaesthetic ethers² is rare; this is due to the fact that the latter are generally supplied to the consumer in sealed tins containing a minimum amount of air. Since it is highly important that ether intended for anaesthetic purposes should be carefully manufactured and properly stored, as prolonged exposure to light and air greatly affect the results of etherization, causing coughing, suffocation, and even dangerous after-effects,³ such ether should always be tested for peroxides and aldehyde, and the presence of the latter should be rigorously guarded against. The same precautions should be taken when the ether is intended for analytical purposes.⁴

The following tests have been proposed for the detection of peroxides (ethyl peroxide and hydrogen dioxide, as well as all other peroxidized compounds) in ethyl ether:

I. TESTS DEPENDENT UPON OXIDATION.

(a) Tests Dependent upon the Liberation of Iodine.

1. *The Test with 10 Per cent. Potassium Iodide Solution.*—Saladin⁵ stated that potassium iodide imparted a yellow coloration to ether if the latter contained sulphuric acid; but Cloez⁶ suggested the employment of the salt as a reagent for ozone. DeVry⁷ found that pure ether has no action upon iodides, and Borrigter found that ether containing hydrogen dioxide liberates iodine from potassium iodide. Poleck and Thümmel⁹ found that the liberation of iodine from iodides,

¹ Others have also found reasons to doubt the existence of vinyl alcohol in ether. Abraham (*J. Soc. Chem. Ind.*, **11**, 836) considered its existence as improbable; and Nef (*Ann.*, **298**, 202) mentioned that its identity is not fully established.

² None of the fresh samples of ether of anaesthetic grade examined by the authors contained peroxides. Even two samples in sealed tins which had been exposed to varying temperature conditions for about one year were free from peroxides, and a tin containing 100 g. of ether which had been stored for one year and a half, sealed and unopened, gave no peroxide reaction; and it would appear from our experiences that these substances are only likely to occur in ether which has been stored in badly stoppered containers. In general, then, the fault is that of the consumer and not of the manufacturer, since ether is supplied, as a rule, in vessels which preclude the possibility of considerable amounts of peroxides forming.

³ Buxton's *Anaesthetics*, 1907, 117.

⁴ As an illustration of the importance of guarding against the presence of peroxidized compounds in ether for analytical purposes, this case may be cited: It has been stated that solutions of quadrivalent titanium give a yellow color with ether in the presence of alcohol. This, however, is only the case when the ether contains peroxidized compounds (cf. Stähler *Ber.*, **38**, 2619). See also the experiences of Lunge and von Keler (*Z. angew. Chem.*, **1894**, 670; **1896**, 3; Lunge's *Chem. techn. Untersuchungs-methoden*, 5 Aufl., **1**, 385) and of Stokes and Cain (*J. Am. Chem. Soc.*, **29**, 410) in the colorimetric determination of iron.

⁵ *J. chim. med.*, **1831**, 531.

⁶ *Compt. rend.*, **43**, 38.

⁷ *J. Pharm. Chim.*, December, 1872.

⁸ *Chem. News*, **53**, 69. See also, Houzeau, *Compt. rend.*, **67**, 714, 1138, who had found that "oxygenated water" decomposes KI (1868).

⁹ *Arch. Pharm.*, **1889**, 961.

¹ See Freer, *Am. Chem. J.*, **18**, 558.

² Fuming hydrochloric acid is well known as a test for proteins; and Reichard (*Pharm.-Ztg.*, **55**, 158, 167) has found that 25 per cent. hydrochloric acid also gives a blue color.

³ Feder (*Z. Nahr. Genussm.*, **15**, 234) has found that hydrogen dioxide gives a violet coloration when heated with milk and hydrochloric acid in the presence of formaldehyde. A violet color is also produced when formaldehyde is treated with a protein in the presence of hydrochloric acid (see Voisenet, *Compt. rend.*, **150**, 40).

⁴ The production of aldehydes in cheeses may be attributed to the fermentation of lactose (Trillat and Sauton, *Compt. rend.*, **144**, 495).

⁵ See tests under "Peroxides."

especially in the presence of acetic acid, is due to the presence of hydrogen dioxide; and it is generally recognized, especially since the work of Dunstan and Dymond,¹ that the impurity in ether which liberates iodine is hydrogen dioxide, although several have maintained that ozone is the cause of the reaction.² Ethyl peroxide also causes the separation of iodine from potassium iodide solution,³ and the latter serves for the detection of peroxidized compounds in general in ether. It lacks the reliability required for a specific test, however, and is open to the following objections:

(i) Potassium iodide solutions are decomposed by light.

(ii) Dissolved oxygen may often cause the separation of iodine.

(iii) The presence of sulphurous and sulphuric acids can cause the liberation of iodine; and the test is also interfered with by the presence of chlorine, bromine, and nitrous acid.⁴

It has been stated that perfectly pure ether may liberate iodine from potassium iodide,⁵ but this is incorrect when the proper precautions are observed; and the facts which establish its unreliability⁶ are limited to those enumerated above.⁷

The potassium iodide test is given in the pharmacopoeias of Germany,⁸ Switzerland,⁹ Japan,¹⁰ France and Holland.

¹ *Pharm. J. and Trans.*, [3], **17**, 841. Warden (*Pharm. J.*, [3] **15**, 521) concluded that the liberation of iodine from potassium iodide indicated the presence of aldehyde, and Dunstan and Dymond demonstrated that the impurity which liberates iodine is hydrogen dioxide. Aldehyde is without action on potassium iodide.

² Werner (*Pharm. J.*, [3], **16**, 660) regarded the liberation of iodine from potassium iodide as an indication not of an actual impurity in ether, but of its decomposition under the influence of light and air, whereby ozone is formed; and Buchner (*Chem.-Ztg.*, **9**, 69) stated that ozone is rapidly formed when ether is exposed to light, and that this body is the cause of the liberation of iodine. We have already shown that ozone cannot exist in a free state in moist or "dry" ether.

³ "On the Action of Ozone on Potassium Iodide Solutions," see Brunck, *Z. anorg. Chem.*, **10**, 222; and Garzarolli-Thurnlackh, *Monatsh.*, **22**, 955. "On the Action of Hydrogen Dioxide on These Solutions," see Kingzett, *J. Chem. Soc.*, **37**, 805; and Schöne, *Ann.*, **195**, 228.

⁴ Von Neander, *Chem.-Ztg.*, **26**, 336.

⁵ Allen [*Commercial Organic Analysis*, **1**, 181 (1908)] states that "some specimens of commercial ether liberate iodine from potassium iodide, a reaction which is not improbably due to the presence of traces of ethyl nitrite." This suggestion is not supported by known facts, since, although, as shown by Berthelot, perfectly dry ether can form, on long standing under the influence of air, traces of nitric acid, as well as ethyl peroxide, ethyl nitrite has never been observed in commercial ethers and its formation is, in our opinion, improbable.

⁶ Dunstan and Dymond, *loc. cit.*

⁷ "On the Reliability of the Potassium Iodide Test," see also Schobig, *Apoth.-Ztg.*, **9**, 210; and Leeds, *J. Am. Chem. Soc.*, **1**, 65.

⁸ The potassium iodide test is usually specified as follows: 10 cc. of ether and 1 cc. of aqueous 1:10 potassium iodide solution, when frequently shaken in a well-stoppered bottle, must show no coloration during one hour's exposure to diffused daylight. Krauch and Merck (*Chemical Reagents, Their Purity and Tests*, **1907**, 101) direct that the mixture be shaken vigorously in a completely filled glass-stoppered bottle, and state that neither the ether nor the potassium iodide solutions should acquire a color after standing one hour in the dark.

⁹ The German Pharmacopoeia employs potassium iodide solution, 1 cc. to 10 cc. of ether, and protects the mixture from the light; it is stated that no coloration should result within 3 hours. In this connection, see Hirsch's *Universal Pharmacopoe*, **1**, 29, (1902); *Deutsches Arzneibuch*, 5th revision, **1910**, 34.

¹⁰ The *Pharmacopoeia Helvetica*, **1907**, 25, gives the test with potassium iodide for "vinyl alcohol."

¹¹ The *Pharmacopoeia of Japan*, **1907**, 25, specifies that if 10 volumes of ether and 1 volume of potassium iodide solution be put in a well-stoppered glass bottle, so as to make it quite full, and then set aside, protected from the light, and with frequent shaking, it should acquire no coloration within an hour. According to this Pharmacopoeia (p. 26) narcotic ether should acquire no coloration under the same conditions within three hours. This test is more complete than those usually specified.

We found that pure ether containing 0.01 per cent. of hydrogen dioxide produced a faint coloration with a 10 per cent. potassium iodide solution, when the hydrogen dioxide was added to the ether and thoroughly mixed just before applying the test; but when the ether was allowed to stand in the dark for several days, the coloration was very pronounced. We cannot recommend the test, however, on account of its unreliability.

2. *The Test with Potassium Iodide and Starch Solution.*—Heldt¹ suggested the employment of potassium iodide-starch solution as a reagent for ozone, and this reagent may be used for the detection of peroxides in ether, a blue coloration resulting from the liberation of iodine. In fact, 0.05 mg. of hydrogen dioxide per liter may be detected in an acid solution, and the blue color is visible in solutions containing the iodine yielded by one part of potassium iodide in 600,000 parts of water at 0° C. The test is, however, subject to the same limitations as the potassium iodide test, and even to a greater degree.

3. *The Test with Potassium Iodide and Phenolphthalein Solution.*—This test, which is identical with the one proposed by Houzeau for the detection of ozone, except that phenolphthalein is substituted for litmus, is given by Wobbe² as follows: If 20 cc. of ether are shaken with 5 cc. of a potassium iodide-phenolphthalein solution (a mixture of equal parts of a 50 per cent. solution of potassium iodide and a 1 per cent. solution of phenolphthalein), the latter should not be reddened. Rosolic acid may be employed instead of phenolphthalein.

The action of light and alkali from the glass render this test open to serious objections. It is also disturbed by the presence of acids. The test is, however, an exceedingly delicate one, a pronounced reaction resulting in the presence of the merest traces of peroxidized compounds.

(b) Tests Dependent upon Color Reactions.

1. *The Vanadic Acid Test.*—Jorissen³ proposed the following test for the detection of peroxides in ether: 0.1 gram of powdered vanadic acid and 2 cc. of sulphuric acid are placed in a small porcelain capsule, and the whole is heated for 10 to 15 minutes on the water-bath, and then allowed to cool. The red-brown mass is then dissolved in water and made up to 50 cc.; one or two cc. of this pale yellow reagent are placed in a test-tube, 5 or 10 cc. of the suspected ether are added, and the whole is well shaken. Should peroxides be present, the mixture assumes a color varying from rose- to blood-red. Jorissen found this test more delicate than the perchromic acid test and more rapid than the potassium iodide test. It is specified by the *Pharmacopoea Belgica*⁴ as follows: 10 cc. of ether, when shaken with 1 cc. of vanadic acid solution, should acquire no red color.

We have found that the vanadic acid test is a re-

¹ *Chem. Centr.*, **1862**, 886; see also, Ferriere, *Compt. rend.*, **74**, 17. Potassium periodate may be used in place of potassium iodide in this reagent. In the *Pharmacopoea Nederlandica* (**1905**, 27), the water-extract is tested with potassium iodide and starch solutions.

² *Apoth.-Ztg.*, **18**, 458.

³ *Ann. chim. anal.*, **8**, 201; *Chem.-Ztg.*, **27**, R., 128; *Répert. de Pharm.*, **15**, 167.

⁴ **1906**, 15.

liable and ready one, being of great delicacy and of easy application. When peroxides are present in the ether under examination, a permanent color is afforded which is readily distinguishable, even when the ether contains but 0.003 per cent. hydrogen dioxide. The reagent may be more conveniently prepared by using ammonium metavanadate and sulphuric acid.

2. *The Ferrous Hydroxide Test.*—This test was given by Thoms¹ as follows: In a watch glass dish, let one cc. of freshly prepared ferrous sulphate solution, 1 : 10, be superposed by 10 cc. of ether and let a few drops of "soda solution" be added. The resulting greenish white ferrous hydroxide should not turn brown within one minute. This test was stated to be preferable to the one with potassium iodide.

We have found that an ether containing 0.01 per cent. of hydrogen dioxide gives a slight but decided reaction in a half a minute in this test; but it is less delicate and more liable to errors than the vanadic acid test of Jorissen. Care must be taken that perfect superimposition occurs when the ether is added, else ferric hydroxide may form almost immediately (less than half the time limit of the test).

3. *The Ferrous Sulphocyanate Test.*—Stokes and Cain² found that hydrogen dioxide may be readily detected in ether by shaking it with freshly reduced acidified ferrous sulphate solution to which a sulphocyanate has been added, when ferric sulphocyanate is generated and is taken up by the ether. Since, however, "even the best grades of ether show this behavior unless especially purified," and on account of the many possible sources of error, this test, although of decided theoretical merit, cannot be recommended.

(c) Tests Dependent upon the Formation of Periodides.

1. *The Caffeine Alkylodide Test.*—Rossolimo³ found that ether containing hydrogen dioxide possesses the property of oxidizing caffeine alkylodide to a slight extent, but that the oxidizing power of ethyl peroxide would appear to be a much greater one, as caffeine alkylodide is decomposed by it with copious formation of periodides.

II. TESTS DEPENDENT UPON REDUCTION.

1. *The Chromic Acid Test.*—This test, which originated with Schönbein,⁴ may be given as follows: Some potassium chromate, with a few drops of dilute sulphuric acid, is added to the ether and the mixture is well shaken; a blue color shows the presence of hydrogen dioxide. It is specified in the Pharmacopoeias of Great Britain,⁵ Hungary, Switzerland and France.

Deniges⁶ stated that 0.5 mg. of hydrogen peroxide is the smallest quantity which can be detected by the

¹ *Ber. Pharm. Ges.*, **1894**, 240; *Merck's Annual Report for the Year 1900*, 8, 27.

² *J. Am. Chem. Soc.*, **29**, 409; *Bull. Bur. Standards*, **3**, 115.

³ *Ber.*, **38**, 774.

⁴ *Ann.*, **109**, 134.

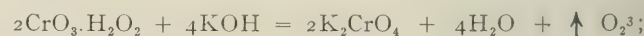
⁵ The British Pharmacopoeia employs potassium dichromate acidified with sulphuric acid, requiring that the ethereal solution shall not develop a blue color. This test is mentioned in the *National Standard Dispensatory*, **1905**, 111. White (*Pharm. J.*, [4], **25**, 780) directs that this test be made thus: Dissolve about 0.1 gm. of potassium dichromate in 9 mls. of water, add 1 mil. of dilute sulphuric acid, and then shake with 2 mls. of ether. After separation, the ether should be colorless.

⁶ *Bull. soc. chim.*, **1890**, 797.

chromic acid test, but Fairley¹ has detected 0.1 mg. by this method. He employed chromic acid solution directly. Dunstan and Dymond² found that it will show the presence of 0.02 per cent. hydrogen dioxide in ether; and we have found that when 10 cc. of an ether containing 0.01 per cent. of hydrogen dioxide are added to 10 cc. of potassium dichromate solution and 2 cc. of sulphuric acid, the ether becomes faintly colored, but no blue color results. With an ether containing 0.02 per cent. of hydrogen dioxide, however, a blue color results at once. This disappears on shaking, and, even when 0.05 per cent. of hydrogen dioxide is present, the ether layer assumes a pale green tint after such treatment. Therefore, since the blue color is not permanent even in an ether containing 5 per cent. of hydrogen dioxide, the test should be specified as follows: A blue color should not result on addition of the ether under examination to the chromic acid solution, and the ether layer, after separation following agitation, should not have acquired a coloration. The blue coloration is due to some such an additive compound as $\text{CrO}_3 \cdot \text{H}_2\text{O}_2$, which is very unstable and has but a brief existence. It is at once destroyed in weak hydrogen dioxide solutions by shaking the mixture. In an acid solution—for example, in the official test of the British Pharmacopoeia for peroxides in ether—the chromic acid is reduced immediately upon the spontaneous decomposition of the additive compound, and green $\text{Cr}_2(\text{SO}_4)_3$ results. The blue color is not necessarily prolonged by larger amounts and disappears when small amounts of peroxides are present, by simple agitation. When an ether containing peroxides—for simplicity, one containing hydrogen dioxide—is mixed with a potassium dichromate solution acidified with sulphuric acid, the ethereal layer is colored blue from the temporary solution of the compound formed, if the amount of hydrogen dioxide present amounts to or exceeds 0.2 per cent. On mixing by agitation, this reaction occurs:



This is confirmed by the fact that ferrous salts are oxidized by the ethereal liquid containing the blue substance in solution and that alkalies decompose it to alkali chromates and oxygen,



and by the fact that the ethereal solution evolves oxygen when evaporated, and CrO_3 remains.⁴

Owing to its comparative lack of delicacy and the instability of the blue coloration indicative of the presence of peroxides, this test is less preferable than the vanadic acid test and should only be employed for confirmatory reasons.

2. *The Potassium Ferricyanide-Ferric Chloride Test.*—Potassium ferricyanide-ferric chloride solu-

¹ *Chem. News*, **62**, 227.

² *Pharm. J.*, **17**, 849.

³ See Moissan, *Compt. rend.*, **97**, 96; Martinon, *Bull. soc. chim.*, [2] **45**, 862.

⁴ Aschoff (*J. prakt. Chem.*, **81**, 401, 487), Barreswill (*Ann. chim. phys.*, [3] **20**, 364), Schönbein (*Pogg. Ann.*, **108**, 471; *J. prakt. Chem.*, **70**, 257), Lenssen (*Ibid.*, **81**, 278), and particularly Bach (*Ber.*, **35**, 872) have investigated the action of chromic acid on hydrogen dioxide solutions also.

tion has been recognized as an efficient test for the detection of hydrogen dioxide.¹ Wobbe² has suggested it for determining the presence of peroxides in ether as follows:

If 20 cc. of ether are shaken with 5 cc. of a freshly prepared potassium ferricyanide-ferric chloride solution (two drops of a ferric chloride solution free from acid and of a specific gravity of 1.280 to 1.282, diluted to about 90 cc., a freshly prepared potassium ferricyanide solution added drop by drop until the liquid acquires a "wine-yellow" color, and the whole made up to 100 cc.), the aqueous liquid, in the dark, should acquire neither a green nor a blue color.

Since other substances (SO_2 , etc.) will reduce ferricyanide to ferrocyanide, this reaction cannot always be relied upon. Some of the higher aldehydes will also give the same reaction as hydrogen dioxide with potassium ferricyanide-ferric chloride solution.³

Jorissen's vanadic acid test is the most satisfactory test of those which have been proposed for the detection of peroxides in ether. When the other tests are applied, the presence of such substances as interfere with the reaction must be carefully guarded against, and this is not always possible. The limitations of these tests and the need of more reliable reagents for the detection of peroxides in ether induced the authors' endeavor to devise more appropriate tests, and the results of this inquiry follow.

VI. (b) SOME SUPPLEMENTARY TESTS FOR THE DETECTION OF PEROXIDES IN ETHER.

Quite a number of tests have been proposed for the recognition of hydrogen dioxide. We have, for example, the well known guaiacum-malt test,⁴ and sulphuric acid solutions of ammonium molybdate, and titanous acid,⁵ various aniline bases,⁷ lead and copper hydroxides,⁸ dimethyl-paraphenylenediamine, phosphorus tribromide-copper nitrate,⁹ and the benzene solution of the cobalt salt of naphthenic acid,¹⁰ have also been employed for the detection of hydrogen dioxide. None of these tests has been proposed for the detection of peroxides in ether, and this would appear to be due to the following reasons: (1) some are not applicable in ethereal solutions; (2) others lack the delicacy necessary for the detection of hydrogen dioxide in very dilute solutions; (3) some of the reagents are uncommon, and this would result in inconvenience to the worker.

It is well known that *cobaltous hydroxide* changes to a brown color through oxidation, going over into *cobaltic hydroxide*; and it would seem, therefore, that either

a cobalt or manganese¹ salt could be employed in the -ous form in place of ferrous sulphate in the test proposed by Thoms for the detection of peroxides in ether.

Schmatolla² found that when 200 cc. of the solution to be tested are acidified with a few drops of dilute sulphuric acid, and about the same quantity of a 1 per cent. cobalt nitrate solution is added, a sharp brown coloration results on adding potassium hydroxide solution if hydrogen dioxide is present. This test was found capable of detecting hydrogen dioxide in a dilution of 1 : 1,000,000. Ditz³ suggested employing a solution of cobaltous oxide in concentrated potassium hydroxide as a test for peroxides in ether, finding that the blue color disappears if peroxides are present in even minute amounts.

We have found that the presence of 0.003 per cent. hydrogen dioxide may be quickly and easily detected in ether by adding three drops of dilute sulphuric acid and the same amount of a 1 per cent. solution of cobalt nitrate to 25 cc. of the ether, then adding potassium hydroxide solution and shaking. A brown precipitate is produced under these conditions, whereas if pure ether is used, a white precipitate results. Acetaldehyde is without action on the precipitate.

A *cerous salt* may be similarly used for the detection of peroxides in ether. On shaking 5 cc. of a 10 per cent. cerous nitrate or cerous chloride solution, rendered barely alkaline with ammonium hydroxide, with 25 cc. of the ether, the white cerous hydroxide should not assume a darker tint. The cerous hydroxide must be prepared just prior to performing the test and must not be allowed to stand in the air. The test is most satisfactorily conducted in an almost completely filled bottle, and the observation as to color should be made by comparison with a blank test on pure ether immediately after shaking one minute. Ether containing 0.003 per cent. of hydrogen dioxide will cause the cerous hydroxide to assume a yellow color, while larger amounts cause varying shades of color from yellow to dark orange; the precipitate resembles ferric hydroxide. Ammonium carbonate solution may be advantageously employed in the place of ammonium hydroxide in this test, since it may be added to the acidified cerous salt solution upon which the ether to be examined is superimposed, and thus the carbon dioxide liberated will expel all air in the bottle in which the test is being conducted.

Fairley⁴ showed that in very dilute solutions 0.5 to 0.25 mg. of uranium may be detected by means of the reaction between *uranium nitrate* and hydrogen dioxide. However, he only observed the time required for precipitation, and made no experiments with a view of devising an easily applied colorimetric test.

Aloy⁵ found that on adding to the solution of any uranium compound a little hydrogen dioxide and then potassium carbonate, either solid or in a very concentrated solution, a fine red coloration is developed.

¹ In fact, manganous chloride and manganous acetate papers are well known as being suitable for detecting nascent oxygen and ozone, respectively.

² *Pharm.-Ztg.*, **50**, 641.

³ *Chem.-Ztg.*, **25**, 109.

⁴ *Chem. News*, **62**, 227.

⁵ *Bull. soc. chim.*, [3] **27**, 734.

¹ Weltzien (*Ann.*, **138**, 129) observed that $\text{K}_4\text{Fe}(\text{CN})_6$ becomes $\text{K}_3\text{Fe}(\text{CN})_6$ in the presence of hydrogen dioxide, and Schönbein (*J. prakt. Chem.*, **79**, 67) found that 0.02 mg. of hydrogen dioxide may be detected by this method. Barralet (*Chem. News*, **79**, 136) stated that one cc. of a 1/165000 solution of hydrogen dioxide is sufficient to intensify the pale blue color of ferrous ferrocyanide in 20 cc. of the fresh compound.

² *Loc. cit.*

³ Cf. Molinari and Fenaroli, *Ber.*, **41**, 2789.

⁴ Schönbein, *J. prakt. Chem.*, **105**, 219; Houzeau, *Compt. rend.*, **66**, 44.

⁵ Denigès, *Compt. rend.*, **110**, 1007; Crismer, *Bull. soc. chim.*, [3] **6**, 22.

⁶ Richarz, *Pogg. Ann.*, **31**, 912.

⁷ Ilosvay, *Ber.*, **28**, 2029; Denigès, *J. Pharm.*, [5] **25**, 591.

⁸ *Analyst*, **15**, 120.

⁹ Christomanos, *Verh. Ges. Deut. Naturf. Aerzte*, **1905**, II, 76.

¹⁰ Kharichkov, *Chem.-Ztg.*, **34**, 50.

The addition of alcohol, he found, resulted in the precipitation of the unstable red compound.

We have ascertained that this test may be suitably elaborated and employed for the detection of peroxides in ether. On adding 5 cc. of a 5 per cent. solution of uranium nitrate, previously saturated with either sodium carbonate or potassium carbonate, to 25 cc. of ether and thoroughly shaking, the greenish yellow color of the uranium solution should not be changed. If the ether under examination contains 0.01 per cent. of hydrogen dioxide, a yellowish brown color is assumed by the uranium solution, and this may be readily distinguished by comparison with a blank test made on an ether of known freedom from peroxides. Even the presence of 0.003 per cent. of hydrogen dioxide causes the production of a sharp orange color, while the presence of considerable amounts produces a red coloration. In fact, the color grades from a golden color to red, according to the amount of impurity present. Acetaldehyde in no way interferes with this test.

Arnold and Mentzel¹ found that hydrogen dioxide can be recognized in the presence of ozone by means of a solution of *benzidine* and *copper sulphate*, which gives a blue precipitate with hydrogen dioxide, but only a reddish yellow precipitate with ozone; and, according to Molinari and Fenaroli,² the benzidine reaction is the best test for hydrogen dioxide in the presence of aldehydes.

In order to ascertain whether this test is applicable in the case of ether, a saturated solution of benzidine (Merck's H. P.; m. p. = 122°) in pure ethyl alcohol and a 10 per cent. solution of pure copper sulphate were employed. When several drops of each of these solutions are added to pure ether, a brick-red separate results upon agitation; but in the presence of hydrogen dioxide, this changes to a blue or greenish color, varying generally from grayish green to greenish black, depending on the amount of peroxide present, and in the presence of considerable amounts of hydrogen dioxide the separate possesses a brownish black color. Benzidine is usually slightly oxidized and the pure substance should be used. Acetaldehyde is without apparent action when present and causes no alteration in color.

This test, besides being easily applied, is productive of a marked color change in the presence of minute amounts of hydrogen dioxide, and is to be recommended for the detection of peroxides in ether.³

The Reactions of Hydrogen Dioxide with Various Iodides.

The unreliability of the potassium iodide test for the presence of hydrogen dioxide and ethyl peroxide in ether caused us to investigate the deportment of various metallic iodides with "ozone" ethers of various strengths, in order to ascertain whether any of them would serve as delicate and reliable reagents for the detection of these impurities of badly-stored

ether. The iodides were considered the most promising, in the case of stable compounds, on account of their ready oxidation and the fact that the separation of free iodine imparts a coloration which is readily determinable even in very minute amounts, Kastle⁴ having found that 0.000066045 g. of iodine is sufficient to impart a distinct yellow color to 20 cc. of water.

Schönbein⁵ found that the addition of a few drops of lead acetate solution, followed by potassium iodide and starch, and a little acetic acid produces a blue color in the presence of hydrogen dioxide. He also found that when hydrogen dioxide is added to a solution of zinc or potassium iodide and ferrous sulphate, iodine is set free, indicated by the formation of blue iodide of starch. Although it has a delicacy of 1 in 25,000,000 parts, this test is only suitable for neutral solutions. Traube⁶ adds a small quantity of copper sulphate in acid solutions.

Caffeine alkyl iodide and the double iodides of lead and ammonium, lead and potassium, and potassium and mercury, cannot be used as reagents for peroxides, as they decompose in the presence of moisture.

Directly bearing upon the subject under consideration is the test proposed by Buchner⁷ for the detection of ozone in ether. Buchner found that cadmium iodide forms cadmium oxyiodide and free iodine in the presence of ether containing ozone (sensitive to 0.05 per cent.), but he failed to consider the action of hydrogen dioxide and of ethyl peroxide on this salt, although he stated that hydrogen dioxide is formed in ether in the presence of water and that oxidation occurs after some time.

In view of the possibilities presented by the iodides as reagents for the detection of peroxides in ether and the fact that these have received little consideration so far in this connection, it seemed desirable to examine the action of ether containing known amounts of hydrogen dioxide with the following iodides: cadmium potassium iodide, the iodides of arsenic, lead iodide, stannous iodide, zinc iodide, and calcium iodide.

From the results obtained in the preliminary tests, it was concluded that only cadmium potassium iodide, lead iodide, stannous iodide, and zinc iodide might be suitable as reagents for the detection of peroxidized compounds in ether.

A 10 per cent. solution of cadmium potassium iodide was prepared. This solution acquired a yellow color in the presence of hydrogen dioxide, but was unaffected by sulphuric or acetic acids and by acetaldehyde. On adding several cc. to a 0.01 per cent. solution of hydrogen dioxide in pure ether, a decided reaction occurred at once on shaking and the ethereal layer assumed a yellow color. With a 0.0025 per cent. solution of hydrogen dioxide in pure ether, a faint, yet distinguishable, coloration resulted on shaking. 10 cc. of ether and 2 cc. of the reagent were used.

Since a 10 per cent. potassium iodide solution assumes a pronounced yellow color in one hour on exposure to sunlight, and a decided coloration in even 30 minutes,

¹ Ber., **35**, 2902.

² Ibid., **41**, 2789.

³ Wilkinson and Peters (*Z. Nahr. Genussm.*, **16**, 172) have devised a test for the detection of hydrogen dioxide in milk, using benzidine.

⁴ Am. Chem. J., **21**, 398.

⁵ J. prakt. Chem., **86**, 129; see also, Struve, *Z. Chem.*, **1869**, 274.

⁶ Ber., **17**, 1062.

⁷ Chem.-Ztg., **9**, 69; Ber., **1885**, 376.

whereas, a 10 per cent. cadmium potassium iodide solution remains perfectly colorless and is not decomposed on like exposure, and since the latter is unaffected by any likely amounts of acids in ether, yet possesses great delicacy and is easy to apply, its use is preferable to potassium iodide as a reagent for peroxides in ether, and we can recommend it for the purpose.

Lead iodide is by no means so suitable. On account of its insolubility, this salt is not advantageous to use alone, yet its deportment with ether containing hydrogen dioxide was determined.

Hydrogen dioxide in considerable amounts was found to decompose lead iodide, the ether assuming a brown color.¹ When a small amount of the salt was added to a 0.01 per cent. solution of hydrogen dioxide in pure ether (0.5 g. PbI_2 to 10 cc. of ether), and the mixture was thoroughly shaken, the ether layer assumed a yellow color; however, no reaction occurred when a 0.0025 per cent. dioxide solution was used. Since all the double iodides of lead, except those with the quaternary ammonium bases, are decomposed by water, none of these possess signal advantages over lead iodide.

Stannous iodide was found to dissolve in ether, forming a red solution. When water was added to this and the mixture was well shaken, the ethereal layer assumed a yellow color and the aqueous layer became turbid. The addition of hydrogen dioxide produced a dark brown color in the ethereal layer. A test for peroxides in ether may be applied with this salt as follows: Dissolve 0.5 g. of the iodide in 20 cc. of pure ether, and then dilute the red solution with an equal amount of water, when an almost gelatinous pale yellow mixture should result. An equal quantity of the ether to be examined is added to this mixture, and, upon thorough agitation, the ethereal layer, after separation, should be pure white in color. This test will detect minute traces of peroxides, the coloration resulting from an ether containing 0.0025 per cent. hydrogen dioxide being very marked. It is not to be preferred to the cadmium potassium iodide test, however.

Arnold and Mentzel² pointed out that the zinc iodide and starch test for ozone is not sufficiently characteristic and is interfered with by chlorine, bromine, nitrous acid, and hydrogen dioxide. Zinc iodide, in an anhydrous state, absorbs water and deliquesces, and takes up oxygen from the air, with the liberation of iodine. It is rather a delicate test for the presence of peroxides in ether, but is neither so characteristic nor so delicate as the cadmium potassium iodide test.

VI. (c) ON THE OCCURRENCE OF ACETAL IN ETHYL ETHER.

It is possible that acetal (di-ethyl-acetal) occurs in many, if not all, commercial ethers, especially those which have been carelessly manufactured or stored. The occurrence of acetal in commercial ether may be accounted for in two ways:

¹ The reaction is similar to that which occurs when moist lead iodide is exposed to direct sunlight in contact with air. This would seem to suggest that the formation of hydrogen dioxide induces the decomposition of the salt under such conditions.

² *Ber.*, **35**, 1324.

1. As a primary impurity. Acetal is well known as an impurity of raw spirit, and is formed in this case, as indicated by Döbereiner,¹ Liebig,² Stas,³ and Wurtz,⁴ by the imperfect oxidation of alcohol. It is likely, however, that any acetal existing in alcohol used for the manufacture of ether would be destroyed during etherification, although small amounts, at least, could be again formed by the action of sulphuric acid on alcohol containing aldehyde,⁵ or as a product of the probably limited amount of oxidation which occurs during etherification.⁶

2. As a product of the slow oxidation of alcohol present in ether, such oxidation occurring during imperfect storage. We are unprepared at present to give direct proofs from which the existence of acetal in ether may be adduced.

"It may be mentioned here that samples of acetal (Kahlbaum's pure) examined by us readily liberated iodine from potassium iodide and cadmium potassium iodide solutions, and oxidized cerous hydroxide. They also gave a coloration with vanadic acid solution; but gave no reaction with Aloy's uranium test-solution or benzidine-copper sulphate solution thus differing from a hydrogen dioxide solution. They possessed a slightly acid reaction, but the presence of acetic acid did not give rise to the reactions in the case of the iodide solutions, since cadmium potassium iodide is very stable towards acids. Therefore, since acetaldehyde is without action on this solution, the reaction could only have been caused by the presence of a peroxidized compound (peracetic acid or aldehyde peroxide) or by the acetal itself. For the present, we are inclined to attribute the deportment to the presence of the former."

VII. (a) TESTS FOR THE DETECTION OF ACETALDEHYDE IN ETHER.

As has been mentioned, acetaldehyde may form in ether during storage, and several⁷ have found occasion to emphasize the objectionable presence of aldehyde in many ethers on the market. It is, therefore, very important that anaesthetic ether be examined for acetaldehyde, an impurity which, when present in "excessive amount," would seem to give rise to respiratory irritation during anaesthesia.⁸

The Potassium Hydroxide Test.—Weidenbusch⁹ in-

¹ *Ann.*, **1**, 185; *Gmelin's Handb.*, **4**, 805.

² *Ann.*, **5**, 25; **14**, 156.

³ *Ann. chim. phys.*, [3] **19**, 146.

⁴ *Ibid.*, [3] **48**, 370; *Ann.*, **108**, 84.

⁵ Delepine (*Compt. rend.*, **132**, 331) has found that the laws regulating the production of acetals are similar to those observed in the analogous cases of esterification and hydrolysis. Acids are peculiarly efficacious in facilitating the reaction, and the nature of the acid and its concentration, if the latter is not too great, are without influence on the result.

⁶ We are of the opinion that during initial action in etherification various oxidation products of alcohol result; that is, that strong sulphuric acid plays the same, or a similar, rôle as when it acts on metals. Many facts lend support to this view.

⁷ Thoms, *Pharm.-Ztg.*, **1894**, 777; Warden, *Pharm. J. and Trans.*, **1885**, 521; *Am. J. Pharm.*, **57**, 148; and Graham, *Proc. Penn. Pharm. Assn.*, **1906**, 153.

⁸ Acetaldehyde vapor, when inhaled, produces asphyxia. Prolonged exposure to light and air gives rise to aldehyde in ether, and such treatment greatly affects the results of etherization. In one case of which we have record, a sample of ether which induced irritation of the respiratory tract during etherization was examined and the only impurity found was acetaldehyde.

⁹ *Ann.*, **66**, 153.

licated that aldehyde forms a resin with aqueous potassium hydroxide, and this observation was later utilized for the detection of an impurity of ether, which, until quite recently, was found to commonly occur, sometimes in considerable amounts, in all ethers on the market. Traub¹ stated that ether suitable for anaesthesia should undergo no change when placed in contact with caustic potash for twelve hours; and it has been specified that 30 cc. of ether and about 5 g. of solid potassium hydroxide, after standing for one day in a dark place and being occasionally shaken, must show no appearance of a brownish substance having separated out. Some, however, consider that a much shorter time limit should be placed. White² recommends that 5 g. of potassium hydroxide in stick form be added to 20 cc. of ether in a stoppered bottle, and that the mixture be then shaken and set aside for two hours; and Krauch and Merck³ direct that on covering pieces of potassium hydroxide the size of a pea with the ether, and setting aside in the dark for one-half hour, the liquid must not acquire a yellow color.

The potassium hydroxide test is specified by the Pharmacopoeias of Great Britain, Germany, United States, France, Holland, Hungary, Spain, Switzerland, Japan, and Belgium. It has, therefore, attained wide recognition.

The British Pharmacopoeia⁴ and the German Pharmacopoeia use the solid form of potassium hydroxide, and the Pharmacopoeia of the United States the solution. The British Pharmacopoeia gives neither a time limit nor the quantities to use; the Pharmacopoeia of the United States uses 10 cc. of ether and 1 cc. of potassium hydroxide (T.S.) and a time limit of one hour, while the German Pharmacopoeia requires that 20 cc. of "narkoseäther," when allowed to stand over solid potassium hydroxide in the dark, shall afford no yellow color within six hours; in the case of ether not intended for anaesthetic purposes, the time limit is placed at one hour. *The National Standard Dispensatory*⁵ specifies the test according to the Pharmacopoeia of the United States.

The Pharmacopoeias of Germany, Holland and Switzerland⁶ state that the test with potassium hydroxide is for the presence of "vinyl alcohol" as well as of aldehyde. The Pharmacopoeia of Japan⁷ states that if ether "be sprinkled upon newly ground potassium hydroxide, and set aside tightly closed and protected from the light, the latter should not assume a yellowish color within half an hour;" and that if narcotic ether "be sprinkled upon newly ground potassium hydroxide, and allowed to stand tightly closed and protected from light, the latter should not acquire a yellowish color within six hours."⁸ The latter test is almost identical with the German requirement, and is more reliable than the test given in the United States Pharma-

copoeia. The *Pharmacopoea Belgica*¹ specifies that "20 cc. of ether and about 4 g. of fragments of sodium hydroxide should assume no yellow color when allowed to stand one-half hour in the dark." This test is less rigorous in requirements than the German and Japanese.

Traub,² Vulpius³ and Schobig⁴ have investigated the deportment of potassium hydroxide with ether, but it would appear that others have found reasons to state that impurities other than aldehyde will impart a yellow or brown color to commercial ether on the addition of potassium hydroxide. Poleck and Thümmel⁵ state that "vinyl alcohol" will cause such a coloration, and Borrigter⁶ found that ether containing hydrogen dioxide colors a portion of potassium hydroxide yellowish brown, an observation which had previously been made by Schönbein.⁷ Solid potassium hydroxide is colored an intense orange-brown by ozone,⁸ but peroxides produce no coloration, hence, we are of the opinion that acetaldehyde is the only substance likely to respond to the test with potassium hydroxide when it is applied to ether, except certain organic substances that are referred to later.

"In order to determine this experimentally, 5 g. of potassium hydroxide were added to the following samples of ether, 30 cc. of each being used in the tests:

"1. Ether distilled over sodium, and containing mere traces of acetaldehyde.

"2. An ether containing 0.5 per cent. of hydrogen dioxide but otherwise pure.

"3. An ether intended for analytical purposes; this ether contained small amounts of moisture.

"4. No. 3 after the addition of 3 per cent. of absolute alcohol.

"5. No. 3 after the addition of 0.05 per cent. of hydrogen dioxide.

"6. No. 1 after the addition of 0.05 per cent. of acetaldehyde.

"7. No. 3 after the addition of 0.05 per cent. of acetaldehyde.

"8. No. 3 after the addition of 0.10 per cent. of acetaldehyde.

"9. No. 8 after the addition of 3 per cent. of absolute alcohol.

"After standing 30 minutes, Nos. 6, 7, and 8 possessed a brown color, and No. 9 had assumed a yellow color. At the end of 24 hours, the following results were observed:

"1. Nil.

"2. Clear, uncolored, separate; potassium hydroxide and ether colorless.

"3. Very small amount of a brownish substance.

"4. Brown solution; no colored substance on the potassium hydroxide as in No. 3.

¹ Pharm. Z. Russland, **31**, 504.

² Pharm. J., [4] **25**, 780.

³ Chemical Reagents, their Purity and Tests, **1907**, 101.

⁴ See Squire's Companion to the latest Edition of the British Pharmacopoeia, **1908**, 103.

⁵ **1905**, 111.

⁶ Pharmacopoea Helvetica, **1907**, 25.

⁷ **1907**, 25.

A similar test is prescribed in the Pharmacopoea Hungarica, **1909**, 18.

¹ **1906**, 15.

² Schw. Wschr. f. Chem. u. Pharm., **1892**, No. 3.

³ Apoth.-Ztg., **1894**, No. 1.

⁴ Ibid., **1894**, 22.

⁵ Z. anal. Chem., **29**, 6.

⁶ Chem. News, **53**, 69.

⁷ Ann., **109**, 134.

⁸ Wurtz, Dictionnaire de Chimie pure et appliquée, **721**; Von Baeyer and Villager, Ber., **35**, 3038; and Bach, Ibid., **35**, 3424.

- "5. Clear, uncolored separate; no brownish substance.
- "6. Yellow solution and considerable "aldehyde resin."
- "7. As in No. 6.
- "8. Much more considerable in amount than in No. 6.
- "9. Red-brown solution.

"From these experiments, it was concluded that the yellow or brownish separate is only caused by the presence of acetaldehyde, and in cases where the ether is tinted yellow or brown, this is often due to the presence of alcohol as well as aldehyde, the former dissolving the resin formed by the latter. Peroxides may produce a turbidity, but no coloration or colored separate."

There is a source of error in the potassium hydroxide test, however. Just as spirits stored in casks made of wood containing tannin show a coloration with potassium hydroxide, so do samples of ether containing pieces of cork, the latter being introduced from the stoppers. The coloration in this case is probably due to the presence of quercitannic acid and resinous matter extracted from the cork through contact with ether. An ether containing mere traces of acetaldehyde—that is, aldehyde not detectable by the potassium hydroxide test—may thus become colored when the test is applied, providing it has remained in contact with cork or contains pieces of broken cork, the latter being by no means unusual owing to the form of the neck of the tin containers in use. We have proved these facts experimentally.

Pure or anhydrous ether, carefully stored, gives a negative result with potassium hydroxide, but few anaesthetic ethers on the American market give an absolute non-response when 30 cc. are tested with 5 g. of solid potassium hydroxide. We obtained the following results:

Sample.	Results.
L.....	After 2 hours, a yellowish brown separate; after 24 hours, a marked brown separate. At the end of four days, ether became turbid.
M.....	After 2 hours, ether was turbid and there was a yellowish brown separate; after 24 hours, a marked brown separate. Ether was clear at the end of four days.
N.....	At the end of 2 hours the ether was turbid, but the separate had a darker color than that in M, and was in clots; at the end of 24 hours, the brownish separate appeared larger in amount and darker than in the preceding.
O..... (A known anhydrous ether.)	No colored substance was formed even after the mixture had stood for five days. Ether remained clear.
P.....	After standing 30 minutes, the mixture had a pale yellowish separate, but the ether was clear; at the end of one day, a yellow-brown separate was found. The latter was more pronounced and the ether was turbid at the end of 48 hours.
X.....	After standing 30 minutes, a pale yellowish brown substance was found; ether was clear. Even after 48 hours, ether was clear, but separate became darker in color.
Y.....	After standing 30 minutes, the ether became turbid (white), but no colored substance separated. Ether was still turbid at the end of one day; and at the end of 48 hours ether possessed a yellowish color, but even then no colored substance had formed.

Sample.	Results.
Z.....	At the end of 30 minutes, ether became slightly turbid and a yellowish substance separated. This was considerably increased at the end of one day.
W.....	After standing 30 minutes, ether became slightly turbid, but no colored substance was formed; no separate even after 48 hours but ether was still turbid.

From our experience, we consider that the potassium hydroxide test for the presence of acetaldehyde in anaesthetic ether is sufficiently rigorous and exacting when specified as follows: On covering 5 g. of solid potassium hydroxide, in freshly broken pieces about 5 mm. in diameter, with 30 cc. of the ether, and allowing the mixture to stand for six hours, tightly closed and protected from the light, and occasionally shaking, the potassium hydroxide should not acquire a yellowish or brown color, no colored substance should separate, and the ether should not become turbid or assume any color.

Those ethers which have been carefully purified and which have been properly stored will give a negative reaction in this test; and ether containing more than mere traces of acetaldehyde may be readily recognized. This test is considerably superior to the U. S. P. test for aldehyde. Anhydrous ether should give no response after standing over potassium hydroxide for twenty-four hours.

The Test with Fuchsin Sulphite.—Schiff¹ found that when a dilute sulphurous acid solution of the sulphate, or any other salt, of rosaniline is shaken with a few drops of aldehyde, sulphurous acid is given off; the solution turns red, then violet, and a precipitate is gradually formed. Cazeneuve² learned that rosaniline salts decolorized by sulphurous acid give a violet coloration with an alcoholic solution of form- or acetaldehyde;³ and Müller,⁴ Urbain,⁵ Lefevre,⁶ and von Bitto⁷ have also studied the deportment of aldehyde with Schiff's reagent.

Mohler⁸ found that aldehyde produced a reddish violet coloration in the presence of "rosaniline bisulphite;" but Francois⁹ ascertained that Mohler's reagent will not mix with ether and that it precipitates sodium salts in the presence of the latter. Therefore, he made attempts to find a reagent of similar delicacy which could be used for the detection and estimation of aldehyde in ether, and found that an aqueous solution of sulphurous acid could be employed in place of sodium bisulphite. He also added to the ether, at the moment of making the test, its own volume of 95 per cent. alcohol free from aldehyde. He learned that 5 cc. of pure ether, 5 cc. of pure 95 per cent. alcohol, and 4 cc. of the reagent remained uncolored for fifteen minutes, but when the pure ether was replaced by an ether containing more than $\frac{1}{10,000}$ part of aldehyde, the mixture assumed a red-violet color, the intensity

¹ *Compt. rend.*, **1865**, 45.

² *J. Pharm. Chim.*, **3**, 595.

³ "On the Detection of Traces of Formaldehyde in the Presence of Acetaldehyde by Means of Fuchsin Bisulphite," see Denigès, Paris Academy of Sciences, Feb. 28, 1910.

⁴ *Z. angew. Chem.*, **1897**, 634.

⁵ *Bull. soc. chim.*, **15**, 455.

⁶ *Bull. soc. Ind. Mulhouse*, **1897**, 84.

⁷ *Z. anal. Chem.*, **36**, 369.

⁸ *Mon. Sci.*, **1890**, 893; **1891**, 582.

⁹ *Chem. News*, **76**, 7; *J. Pharm. Chim.*, **5**, 521.

increasing with the content of aldehyde. Based upon this reaction, Francois elaborated a method which may be used for the estimation of aldehyde in ether.

Klar¹ reported that ether distilled over sodium gives an aldehyde reaction with fuchsine sulphite, and Thoms² stated that it was impossible for him to obtain ether which would not restore the color to fuchsine decolorized by sulphurous acid.

All of the ethers examined by us gave a more or less red-violet color with Francois' reagent (220 cc. sulphurous acid, 30 cc. 1 : 1000 fuchsine solution, and 3 cc. sulphuric acid), and even ether which had been distilled over sodium and then purified by means of potassium permanganate in alkaline solution responded, the coloration being exceedingly faint, however. By adding less sulphuric acid to Francois' reagent, its sensitiveness may be exaggerated, even to the extent of becoming colored with pure ether, and this may account for the observations of Thoms. Increasing quantities of sulphuric acid cause this fault to disappear, and care should always be taken to ensure a sufficient amount being present. Anhydrous ether should give only a slight reaction with fuchsine sulphite, immediately upon adding the latter, and the coloration should not be considerably intensified after the mixture is allowed to stand fifteen minutes.

A test similar to the above, but inferior in delicacy, is the one proposed by Blaser,³ who found that a very weak solution of magenta (1 : 100,000) is bleached completely by exposure to sunlight, and that this solution gives very sharp reactions with aldehyde. It would appear that pure acetone will not affect the recoloration of magenta decolorized by sulphurous acid.⁴

The Aldehyde-Ammonia Test.—The test of Liebig⁵ was applied by Adrian⁶ to ether. The latter found that aldehyde-ammonia may be precipitated by passing a current of dry ammonia gas through the ether and may be filtered off. This test will serve for the detection and approximate estimation of quantities of aldehyde varying from 0.5 to 3.0 per cent., and upwards, but lacks the delicacy of the potassium hydroxide and fuchsine-sulphurous acid tests.

The Test with Alkaline Silver Nitrate Solution.—It is well known that aldehyde forms a mirror when heated with ammoniacal silver nitrate solution, and that this reaction affords a delicate test for the presence of aldehyde.⁷ Wobbe⁸ has suggested that aldehyde be tested for in ether as follows: 20 cc. of the ether are shaken with 5 cc. of alkaline silver nitrate solution (8 g. of silver nitrate dissolved in 20 g. of water, plus 30 g. of ammonia solution of specific gravity 0.923 and 10 g. of 30 per cent. sodium hydroxide solution), after which no mirror should form. When ether which had readily responded to the potassium hydroxide test was tested with Wobbe's reagent, a very slight and indefinite mir-

ror resulted on shaking; this was rendered distinct on immersing in boiling water.

The Test with Nessler's Reagent.—Although it has been stated that ether should be completely indifferent to Nessler's reagent, and notwithstanding the fact that this reagent is one of the best tests for the presence of aldehyde (and alcohol), it is impossible to obtain an ether which gives a totally negative reaction when this test is applied.¹ Modified, however, the test is convenient and suitable for the purpose; such a test is specified in the pharmacopoeias of Belgium and Holland. The former² directs that *aether pro narcosi* should not deposit "a red or black precipitate, although it may assume an opalescent yellow color, when 10 cc. are shaken with 2 cc. of Nessler's reagent," and the latter³ states that 5 cc. of ether should produce no reaction with 5 cc. of water and 3 drops of Nessler's reagent within fifteen minutes.

The German Pharmacopoeia now requires that when 10 cc. of anaesthetic ether ("narkoseäther") are agitated with 1 cc. of Nessler's reagent, there should result no coloring or darkening of the mixture, but at the most a faint white opalescence. A response is stated to be indicative of the presence of aldehyde or "vinyl alcohol."

We found that ether distilled over sodium and containing very slight traces (1 : 10,000) of acetaldehyde imparted an opalescent yellow color to Nessler's reagent after shaking, but no precipitate resulted at once; after the mixture had stood for fifteen minutes, however, it became darker and a small amount of a red precipitate settled out. In ethers containing larger amounts of acetaldehyde, a grayish black precipitate was produced immediately on shaking. We therefore think that the tests of the German, Belgian and Dutch Pharmacopoeias are unnecessarily rigid, and consider that it is sufficient to require that no black precipitate is produced, unless pure ether is wanted.

The Test with Meta-phenylenediamine Hydrochloride.—Schiff⁴ found that meta-phenylenediamine hydrochloride may be used as a reagent for aldehyde; Girard and Rocques⁵ devised a method for estimating the quantity of aldehyde in commercial alcohols by means of the salt; and Windisch⁶ studied its deportment with aldehyde in the presence of alkalis and acids.

Meta-phenylenediamine hydrochloride is very easily decomposed. A 1 : 20 water solution of this compound should be colorless and should not be exposed to the air. In preparing this reagent, only nitrite-free water must be used, although aldehyde-free alcohol may be employed instead of water. When such a solution of meta-phenylenediamine hydrochloride is shaken with ether containing 0.05 per cent. of acetaldehyde, a yellowish brown color is imparted to the solution. It serves, however, to detect even smaller

¹ Chem. Ind., 19, 141.

² Ber. Pharm. Ges., 4, 239. In this connection, see also Schönheimer, Pharm. Centralh., 1894, No. 26.

³ Pharm. Centralh., 40, 607.

⁴ Villiers and Fayolle, Bull. soc. chim., 12, 691.

⁵ Pharm. Centr., 6, 639.

⁶ Mon. Sci., 44, 835.

⁷ Many other substances also give this reaction, so it is not reliable.

⁸ Loc. cit.

¹ Cf. Lassar-Cohn, Ann., 284, 266; Rept. Chem.-Ztg., 1895, 58. In this connection, see Crismer, Deutsch Chem.-Ztg., 4, 81; Rept. Chem.-Ztg., 13, 198.

² Pharmacopoea Belgica, 1906, 15.

³ Concerning the requirements of the Ph. Ndl. IV. for *aether pro narcosi* see Weigl, Pharm. Centralh., 47, 397. Feist (Apoth.-Ztg., 25, 104) recommends agitating 5 cc. of ether with 1 cc. of Nessler's solution.

⁴ Ann., 263, 328.

⁵ Compt. rend., 107, 1158.

⁶ Z. Spiritus-Industrie, 9, 619.

amounts, but is decisive only in the absence of peroxides.¹

Since meta-phenylenediamine hydrochloride appeared to be a delicate reagent for the detection of acetaldehyde, it seemed desirable to ascertain the deportment of its ortho- and para-isomers with ether containing acetaldehyde.

When ortho-phenylenediamine hydrochloride is shaken with ether containing considerable amounts of acetaldehyde, the compound becomes converted into a reddish brown oily separate and the ether becomes turbid. It was found, however, that the test may be most conveniently conducted by employing a water solution of the compound. When ether is shaken with a 1 : 20 water solution, the latter should not assume any color on agitating in an almost totally filled bottle. In the presence of acetaldehyde, a yellow to red-brown color is assumed by the solution, depending on the amount of acetaldehyde present. The presence of 0.06 per cent. acetaldehyde in ether may be thus easily detected, the solution of the compound assuming a marked yellow color. Peroxides, however, give a similar coloration, so their absence must be assured. We recommend, therefore, that this test be used only as a confirmatory one. To apply it, 25 cc. of the ether under examination are superimposed on 10 cc. of water and then 0.05 to 0.10 g. of ortho-phenylenediamine hydrochloride is added; the mixture is then shaken. No coloration should result within one or two minutes. The solution should not be exposed to the air or light.

Para-phenylenediamine hydrochloride is by no means so sensitive and reliable a reagent as the preceding. It is readily oxidized by the air, oxygen, and peroxides, and is not so delicate a reagent for acetaldehyde.

No attempt was made to determine the applicability of the other various tests for the detection of aldehydes in general² to the detection of acetaldehyde in ether, as those tried were of ample sensitiveness and sufficiently easy to apply.

VII. (b) THE PURIFICATION OF ETHER FROM ALDEHYDE.

A variety of methods have been devised for the removal of aldehyde from ether, but, as has been mentioned, it is exceedingly difficult to eliminate this impurity completely.

Treatment with potassium hydroxide or metallic sodium serves to remove not only water but also aldehyde, and an ether so treated contains mere traces of the latter impurity. Lassar-Cohn³ has found that ether may be most satisfactorily freed from alcohol and aldehyde, however, by boiling it with a reflux condenser for twenty-four hours with an alloy of potassium and sodium. This alloy is fluid at low temperatures, and is superior to metallic sodium in that it is

not liable to become encrusted with a protective layer of hydroxide and resin.

Ekenberg¹ found that ether, pure enough for most analytical purposes, may be readily obtained from ordinary ether containing water, alcohol, and oxidation products by adding 5 to 10 per cent. by volume of liquid paraffin and then distilling between 40° and 50° C. The paraffin, the boiling point of which lies above 300° C., remains behind in the retort and retains the impurities. The method probably suffices to free ether from acids, peroxides, and badly-smelling substances, but it does not eliminate, by any means, aldehyde.

Adrian² found that distillation removes any acetic acid present in ether, and recommended that the aldehyde be precipitated by passing a current of dry ammonia gas through the ether, when aldehyde-ammonia separates out and may be filtered off. The ether is subsequently purified by treatment with sulphuric acid, which separates ammonium sulphate, and, after filtering off, the ether is distilled over potassium carbonate.

A well-known method of purification of ether from aldehyde is that based upon the action of potassium permanganate in alkaline solution on ether at 18.3° C. The ether is placed in a stoppered liter flask with 200 cc. of a saturated solution of potassium permanganate and 20 g. of sodium hydroxide. After twenty-four hours and frequent agitation, the ether is decanted off and again submitted to the same treatment. The filtered ether is then left for twenty-four hours in contact with a mixture of 50 g. of quicklime and 50 g. of fused calcium chloride, then filtered and distilled. Francois states that this method serves to completely eliminate aldehyde from ether, but we have found that ether so treated gives a faint coloration with the fuchsine-sulphurous acid reagent; there is also considerable loss of ether, no matter how much care is exercised.

Other methods for the removal of aldehyde from ether are the following:

(a) Precipitation with an alkaline mercuric chloride solution; (b) distillation over hydriodic acid; and (c) by means of phenylhydrazine.

The last method serves also to remove acetic acid and acetone.

VIII. (a) SCHEME FOR THE EXAMINATION OF ETHYL ETHER FOR ANALYTICAL AND ANAESTHETIC PURPOSES, WITH PARTICULAR REFERENCE TO THE DETECTION OF AVOIDABLE IMPURITIES.

1. *Specific Gravity*.—Determine the specific gravity by means of a pycnometer at 15° C. (See discussion under *specific gravity*.)

2. *Boiling Point*.—In the case of anaesthetic ether, at least 97 per cent. of the sample should distil over between 34° and 36° C. (at 760 mm.), and none of it should come over above 37°; after the fractionation to this temperature, no residue should remain in the fractionating vessel.

In the case of anhydrous ether, at least 99.50 per cent. should distil off between 34° and 36°, and none should come over above 36°.

3. *Organic Impurities*.—When 20 cc. of the sample are added

¹ *Chem.-Ztg.*, **18**, 1240.

² *Mon. Sci.*, **8**, 835.

¹ In this connection, see Cazeneuve, *Bull. soc. chim.*, [3] **5**, 855.

² These include the sodium nitroprusside test of von Bitto (*Ann.*, **267**, 372), the phenol-sulphuric acid test of Barbet and Jaudier (*Ann. chim. anal. appl.*, **1896**, 325), the various reagents proposed by Istrati (*Bull. soc. sci. din Bucuresci*, **7**, 163), the phenylhydrazine hydrochloride-sodium acetate test of Fischer (*Ber.*, **17**, 572), and the phenylhydrazine oxalate test of Riegler (*Z. anal. Chem.*, **42**, 168). For the most part, these were considered to be deficient in necessary delicacy and applicability.

³ *Ann.*, **284**, 226.

drop by drop to 20 cc. of pure concentrated sulphuric acid, which is kept cooled during the test, and which is contained in a glass-stoppered bottle previously rinsed with concentrated sulphuric acid, the resulting solution should be colorless. The sulphuric acid should be gently shaken after the addition of each drop of ether in order to ensure perfect solution.

4. *Odor*.—When 50 cc. of the sample are allowed to evaporate spontaneously on filter paper, 10 cm. in diameter, contained in a flat porcelain dish, the paper should be odorless after the evaporation of the ether. The latter should be added to the paper in portions in such a manner as to completely moisten it. In the case of a decided odor being imparted to the filter paper, the ether should be rejected, but for further information may be tested for such impurities as "heavy oil of wine," fusel oil, etc.

5. *Residue (Extractive Matter, Odor and Acidity)*.—(1) When 25 cc. of the sample are allowed to evaporate spontaneously in a clean, dry glass dish, the moist residue must possess no odor, and must neither redden nor bleach blue litmus paper; this residue must evaporate completely on a water-bath—that is, there should be no fixed residue.

(2) 100 cc. of the ether under examination are allowed to spontaneously evaporate in a flask until about 15 cc. remain in the vessel. This residue should be free from color and foreign odor, and should comply in full with the following tests: (a) When 5 cc. are allowed to evaporate at room temperature after the addition of 2 cc. of water, the residue should neither redden nor bleach sensitive light-blue litmus paper. (b) When another portion of 5 cc. is allowed to evaporate on a 9 cm. filter paper contained in a porcelain dish, there should be perceptible no foreign odor (amyl compounds, empyreumata, pungent matters, etc.) as the last portions disappear from the paper, and the latter should be left odorless. (c) On the addition of the remaining 5 cc. to 5 cc. of concentrated sulphuric acid, kept cool during the test and contained in a glass-stoppered tube previously rinsed with concentrated sulphuric acid, there should result no perceptible coloration. Anaesthetic ether should comply in full with these tests.

6. *Acidity*.—(1) When 25 cc. of the sample are allowed to evaporate at room temperature after the addition of 5 cc. of pure water the residue should neither redden nor bleach sensitive light blue litmus paper.

(2) When 20 cc. of pure ether are shaken with 10 cc. of pure water and 2 drops of phenolphthalein, the same depth of color should result on adding an equal amount of $N/100$ potassium hydroxide solution as in a test using pure water alone. In the case of ether intended for special analytical purposes, the addition of 0.3–0.5 cc. of $N/100$ potassium hydroxide should produce an alkaline reaction. When more than 1 cc. is required, the ether should be rejected for anaesthetic purposes.

7. *Water and Alcohol (Exclusion Tests for Pure and Anhydrous Ethers)*.—(1) (This test is superfluous, if the ether possesses a correct specific gravity.) A minute quantity of powdered fuchsine (rosaniline acetate), previously dried at 100°C ., is placed in a dry test tube, 10 cc. of the ether are added, and the tube is corked and shaken well. In the case of pure and anhydrous ethers, no amethystine color—even faint—should result. If the coloration imparted to the ether is considerable, the approximate percentage of impurity is determined by Allen's method.¹

(2) When several milligrams of anthraquinone and the same amount of sodium amalgam are added to 10 cc. of the ether there should result no formation of red or green substances. The presence of both water and alcohol may be detected by this test.

8. *Water (Exclusion Tests for Pure and Anhydrous Ethers)*.—

¹ All colorimetric tests should be performed preferably with a colorimeter, having tubes with an internal diameter of 1.5 cm. But other forms of vessels may be used; for example, a ground glass stoppered Erlenmeyer flask, of suitable size for the amounts of liquid prescribed in the test, has been found to answer.

(1) On shaking 1 g. of anhydrous copper sulphate with 20 cc. of ether, the salt should not assume a green or blue color.

(2) In important or doubtful cases, the test with amalgamated aluminum may be used. If the ether contains no moisture and it responds to the tests under "Water and Alcohol," the presence of the latter may be really assumed, especially if the colors are marked.

9. *Water and Aldehyde (Exclusion Test for Pure and Anhydrous Ethers)*.—When 15 cc. of the sample are placed in a perfectly dry test tube and a piece of metallic sodium about 5 mm. in diameter is added, there should result only a slight evolution of gas and the sodium should not possess, after standing six hours, a white or yellow coating and the ether should not be colored or turbid. Only when the ether has been previously treated with sodium will the latter retain a distinct metallic luster at the expiration of the test; otherwise the metal becomes coated with sodium hydroxide. In the presence of aldehyde the sodium hydroxide is more or less colored.

10. *Acetaldehyde*.—(1) Apply the fuchsine-sulphurous acid test of François. Pure ether should not restore the color to fuchsine decolorized by sulphurous acid. The red-violet color should be faint in the case of anhydrous ether.

(2) On covering 5 g. of solid potassium hydroxide, in freshly broken pieces about 5 cm. in diameter, with 30 cc. of the sample, and allowing the mixture to stand for six hours, tightly closed and protected from the light, and occasionally shaking, the potassium hydroxide should not acquire a yellowish color, no yellowish or brown colored substance should separate, and the ether should not become turbid or assume any color. This is recommended as the exclusion test for anaesthetic ether. Pure or anhydrous ether should give no response after standing 24 hours.

(3) In the absence of alcohol, as indicated by the tests for water and alcohol, and confirmed by those given below, the following test may be applied for the detection of aldehyde: When 10 cc. of the sample are agitated with 2 cc. of Nessler's solution, a yellow color or black precipitate is indicative of the presence of aldehyde. Pure ether is indifferent towards this reagent, but it is impossible to purchase ether which does not show a yellow color within 15 minutes. For anhydrous or anaesthetic ether, it is sufficient to require, therefore, that no black precipitate settles out, although the mixture may assume an opalescent yellow color.

11. *Alcohol*.—The occurrence of alcohol may be ascertained as follows:

(1) In the presence of water, a portion of the sample is dried over anhydrous potassium carbonate and then tested, in 10 cc. portions, with (a) rosaniline acetate, and (b) anthraquinone-sodium amalgam.

(2) In the absence of other than mere traces of acetaldehyde, by Lieben's iodoform test.

(3) In the presence of acetaldehyde, by this method. The amount of aldehyde in 25 cc. is approximately determined colorimetrically by François' method. A portion of 25 cc. is then agitated with 25 cc. pure water in a ground glass-stoppered bottle, and the aqueous layer, which will show an increase in volume greater than 10 per cent. of the ether taken depending on the amount of alcohol present, is removed and freed from dissolved ether by careful warming at 40°C ., until ether is expelled. The alcohol in the water is then oxidized by potassium dichromate and sulphuric acid, the aldehyde produced is distilled off, and the amount contained in the distillate is determined approximately colorimetrically. By comparison with the percentage of aldehyde found as originally existing in the ether, the amount of alcohol may be calculated; however, we do not recommend the method as an exact quantitative one, but only as one for arriving at the approximate amount of alcohol contained in ether, and as a confirmatory test.

12. *Peroxides (Exclusion Test for Ether of All Grades)*—When 2 cc. of a 10 per cent. cadmium potassium iodide solution are well shaken with 10 cc. of the sample, there should result no liberation of iodine within one hour. This may be easily determined by adding starch solution, although the yellow color which results in the presence of the merest traces of peroxides is easy to distinguish. The presence of peroxides may then be confirmed by any of the other tests devised by the authors, or by Jorissen's vanadic acid test.

VIII. (b) THE DEGREES OF PURITY OF AMERICAN ETHYL ETHERS USED FOR ANAESTHESIA.

The main impurities contained in American ethers are, beside alcohol and water, acetaldehyde and acids. As previously noted, the presence of small amounts of alcohol is permissible or may even appear necessary; but anaesthetic ethers should contain but mere traces of moisture, and, as has been indicated, it is desirable that they should be absolutely water-free. This would undoubtedly increase the cost of production; however, so long as ether is supplied in small tins of such a size that the contents are used completely at an operation or that not used, being small, may be discarded, and not stored, it is only necessary that the amount of moisture present be reduced to very small percentage.

Acetaldehyde is undoubtedly the commonest contaminant of anaesthetic ether, and its presence may account for some of the observations in practice usually attributed to idiosyncrasy. With regard to the acidity of the various anaesthetic ethers on the American market, it may be said that none of those we have examined contained acid in what may be termed injurious amounts.

The following table will serve to show the comparative purity of three samples of anaesthetic ether, purchased in the open market by an expert anaesthetizer and submitted to us, numbered, and without our knowing the name of the manufacturer:

Test.	D.	E.	F.
Sp. gr. at 25°.....	0.7162	0.7189	0.7161
Odor.....	No foreign odor	<i>Ibid.</i>	<i>Ibid.</i>
Ether distillate.....	98.50%	97.00%	97.50%
Distillate above 36°.....	0.5%	2.00%	1.50%
"Organic impurities"....	None	<i>Ibid.</i>	<i>Ibid.</i>
Relative acidity in			
g. acetic acid in			
100 cc.....	0.0006	0.00015	0.00165
U. S. P. litmus test....	Negative	<i>Ibid.</i>	<i>Ibid.</i>
Residue.....	None	<i>Ibid.</i>	<i>Ibid.</i>
Water.....	Present ¹	<i>Ibid.</i>	<i>Ibid.</i>
Alcohol.....	Present in permissible amount	Excessive	As in No. D
Relative total impurity (Allen's approximate method).....	5.00%	6.00%	5.50%
Peroxides.....	None	<i>Ibid.</i>	<i>Ibid.</i>
Aldehyde.....	Present in permissible amount	<i>Ibid.</i>	Excessive as compared to others

Since the authorization of two denaturant formulas for ether by the Commissioner of Internal Revenue,² we need no longer consider contamination from methyl

¹ In all three samples, the amount of water present was not excessive providing the ether would have been properly stored or at once consumed completely by the user. All the samples were properly canned. The samples of "D" examined possessed a relatively higher degree of uniformity than the samples "E" and "F."

² See Regulations No. 30, Supplement No. 1, United States Internal Revenue, and *Bulletin No. 130*, Bureau of Chemistry, 1910, 163.

alcohol oxidation products, and the general use in this country of special denatured spirit has rendered probable the production of high-grade anaesthetic ether. It only remains for the manufacturer to consider more carefully contamination from acetaldehyde.

It is encouraging to note that only a little over 1 per cent. of the ether consumed in the United States is imported¹ and that the American product is universally recognized as of high grade; however, not sufficient attention has been given to the storage of ether by the consumer, and until the latter coöperates with the manufacturer, fully and knowingly, the results obtained may continue to be variable, and rigid requirements on the part of the producer are useless. Ether freed from moisture and all but traces of aldehyde by means of sodium or other methods is not required in this country for anaesthetic purposes, and it is generally considered satisfactory if no "after-effects" are observed.

VIII. (c) VALUE OF CHEMICAL TESTS FOR ANAESTHETIC ETHYL ETHER.

The authors feel that the great lack of uniformity among the pharmacopoeias of the world need not obtain, especially where the analytical methods are involved. True, as Remington maintains, "The Pharmacopoeia is a book of standards for medicines, and not for analytical chemists," yet the methods of standardizing should be comprehensive, accurate, and reliable, as well as rapid and as simple as possible. It is unquestionably impossible for every pharmacist to determine the quality of his chemicals and drugs, but the druggist may easily apply simple tests to determine their purity, especially when these tests are decisive and simple; and he should, like the physician, be familiar with the changes which chemicals undergo when improperly stored, in order that he may not allow impurities to develop and may guard against their formation.

Leffmann has stated that tests may in all cases be improved and supplemented by the knowledge of the worker or by resorting to chemical or pharmaceutical literature. This is, as a rule, no doubt true for him who has the training, time and facilities at his disposal; but desirable and necessary literature is not available to all who at times deem it advisable to test their chemicals and drugs. The legal recognition of the Pharmacopoeia, especially that of our own country, renders it all important that inaccuracies be corrected, and improved and omitted methods be included, where necessary, so that these are available to those required to resort to an official work to assure themselves of the quality of the drugs they may use or dispense. The practical difficulty of putting forth frequent editions at short intervals of the entire Pharmacopoeia may be overcome by the issuance of annual supplements. What a step modern civilization would take if the leading nations decided to issue an international standard pharmacopoeia, revised in full each decennium, with annual supplements in the meantime!

¹ No consideration is taken of the ether consumed in the establishments where manufactured. About three-fourths of the ether produced in the United States is used by the manufacturers themselves.

In the case of ether for anaesthetic purposes, some pharmacopoeial tests are unnecessarily rigid; some are open to improvements; others should be replaced entirely by improved methods of detection; and several should be incorporated for detecting impurities not considered.

Furthermore, the demand for a good ether for anaesthesia involves difficulties inherent in the practical application of chemical methods by hospitals and physicians. As has been stated, anaesthetic ether should be provided in small containers, and it is impracticable, and should be unnecessary, to test the contents of each container before use; hence, reliance, as is the common practice now, must be placed on the experience and integrity of the manufacturer and on the uniformity of his product, for we have found that some ethers of the market vary not only in specific gravity and absolute ether content, but also in impurities, from time to time, yet they may comply with the requirements of the Pharmacopoeia.

Finally, in regard to anaesthetics in general, there is no doubt that, though even the most improved chemical and physical tests may be stated ever so clearly in print, and may properly serve to eliminate low-grade material, yet clinical experience must have the final word.

COLLEGE OF THE CITY OF NEW YORK,
1910.

THE ESTIMATION OF LIME AND POTASH IN THE ASH OF CEREALS.

By FIRMAN THOMPSON AND H. H. MORGAN, JR.

Received January 25, 1911.

In the course of some experimental work with cereals being carried on at this station the analysis of a large number of samples of the ash of corn and wheat grains was found to be necessary. During the prosecution of this work it was found that the A. O. A. C. methods, as given in *Bull. 107* of the Bureau of Chemistry, left much to be desired with respect to accuracy as well as rapidity of execution. Our efforts were then directed to removing these defects by modifications of these or other existing methods with a view to increasing the speed while not sacrificing any of the accuracy of the standard methods. We have met with such success in the estimation of potash and lime that we are prompted to publish them at this time, and while not claiming originality for the basic principle involved, we believe that our modifications are very vital to their rapid and accurate execution and trust that they may receive a thorough testing in laboratories other than our own.

CALCIUM OXIDE.

In the A. O. A. C. method for the determination of CaO in plant ash it is necessary to add sufficient FeCl_3 to combine with all of the P_2O_5 present, and the combined phosphates of iron and aluminum are then removed by precipitation with ammonia or an alkali acetate. The ash of cereal grains consists in great part of potassium phosphate, the P_2O_5 amounting to from 40 to 50 per cent. and the K_2O to about 30 per

cent. while the CaO is comparatively low. It is quite obvious that a sample containing sufficient CaO for accurate determination would require a large amount of FeCl_3 to combine with all of the P_2O_5 . In an ash containing 40 per cent. P_2O_5 and 2 per cent. CaO, which is about the average for wheat grains, the amount of iron required to combine with the P_2O_5 would be about fifteen times the amount of CaO and the resultant precipitate of ferric phosphate would amount to about forty times the amount of CaO present. Granting that none of the CaO would combine with the P_2O_5 under such conditions the danger of mechanical loss by absorption is quite apparent to say nothing of the inconvenience of handling such a large precipitate and filtrate. That this danger is a very real one has been the experience of every chemist in this laboratory who has used the method, the results being uniformly low even after repeated re-solution and reprecipitation, as some of the following figures will show.

In devising a method for the determination of CaO which would be free from these objections, advantage was taken of the fact that calcium and magnesium phosphates are very easily soluble in dilute acetic acid while the phosphates of iron and aluminum are quite insoluble.

Method.—50 cc. of the hydrochloric acid solution of the ash, corresponding to 0.500 g., are heated to boiling, made slightly ammoniacal and then acidified again with acetic acid, adding about 10 cc. of 50 per cent. acetic acid in excess, making the total volume not more than 75 cc. The precipitate is boiled for a few minutes, allowed to settle and the combined phosphates of iron and aluminum filtered off and washed thoroughly with hot water. Since this precipitate is usually very small a reprecipitation has not been found necessary. About 10 cc. of saturated ammonium oxalate solution are added to the filtrate while still hot and the CaO determined in the usual way, either by ignition or titration with permanganate.

In order to test the method, known amounts of calcium carbonate and calcium phosphate and potash alum were dissolved and the CaO determined in the solution according to the above method with the following results:

CaO present. Gram.	CaO found. Gram.
0.13475	0.1353
0.13517	0.1348
	0.1345

When large amounts of Al_2O_3 are present a reprecipitation of the AlPO_4 will be necessary as is shown by the analysis of a solution containing 0.0273 g. Al_2O_3 and CaO in the form of chloride and phosphate.

CaO present. Gram.	CaO found with one precipi- tation of AlPO_4 . Gram.	CaO found with reprecipi- tation of AlPO_4 . Gram.
0.1460	0.1383	0.1462
0.1460	0.1329	0.1462

A comparison of the percentages of CaO found in a number of samples of the ash of wheat grains by the two methods is shown in the following table:

FeCl₃ method.

1.55
1.24
1.34
1.33
1.03
0.93
0.83
1.14
0.72
0.62
0.83
0.72

Acetic acid method.

2.27
2.43
2.43
2.56
2.43
2.68
2.76
2.96
2.88
2.43
2.47
2.27

It will be noted that while the results are considerably higher by the acetic acid method they also show a greater uniformity, as might be expected with samples of such similar origin.

It should also be stated here that, although aluminum is commonly supposed to be a comparatively rare constituent of plant ash, we have found a quite appreciable amount in every sample of ash of wheat straw and grains examined by this method. A more complete account of its occurrence will be given later.

POTASSIUM OXIDE.

As is well known the standard method for the determination of K₂O, although quite accurate, is a very long and tedious one, involving as it does the removal of all other bases with the exception of sodium and also requiring, where a large number of determinations are to be made, a large stock of platinum chloride. For these reasons a shorter, more inexpensive method is very much to be desired and our attention was directed to the cobaltinitrite method of Adie and Wood¹ as possibly overcoming the faults mentioned. In working with this method it was found that the best results were secured by allowing the precipitate of potassium cobaltinitrite to crystallize out from the cold acetic acid solution by standing for at least twelve hours, decomposing the precipitate with an alkali, filtering off the cobaltic hydroxide thus formed, cooling the solution and titrating with acidified permanganate. A serious difficulty was met with in the fact that in using a fixed alkali for the decomposition it was almost impossible to effect a complete precipitation of the cobalt, which presumably passed the filter as soluble double salts. As the presence of any cobalt would vitiate the titration with permanganate, it seemed necessary that some other means for the decomposition of the cobaltinitrite should be found. Since the alkaline earths do not have the same tendency to form double salts with cobalt, a saturated solution of Ba(OH)₂ was substituted for the NaOH, and it was found that the precipitation was very complete and the barium sulphate formed in the subsequent treatment interfered in no way with a sharp end reaction. It was also found advisable to titrate by allowing the alkaline solution of the nitrite to run into the hot, acidified, standard permanganate. While this procedure has the disadvantage that the end point must be judged by the disappearance of the color, this is more than compensated for by the elimination of danger of loss of nitrous acid. With a little practice it has been found that it is quite easy to determine the end within one or two drops.

Method.—The hydrochloric acid solution of 0.500 g. of ash is neutralized with NaOH and acidified again with acetic acid, adding 10 cc. of 50 per cent. acetic acid in excess. The solution is boiled and the precipitate of iron and aluminum phosphates filtered off and washed thoroughly with hot water. The filtrate is concentrated to about 75 cc. and allowed to cool. 25 cc. of cobaltinitrite solution, made according to the method of Adie and Wood, given below, are now added. Allow to stand over night at the room temperature and filter on an asbestos felt in a Gooch crucible, washing several times with cold, 10 per cent. acetic acid and finally once with cold water. The asbestos and precipitate are transferred with water to a small beaker, 40 cc. of a saturated Ba(OH)₂ solution added and heated to boiling when a copious precipitate of cobaltic hydroxide will be formed. Allow the precipitate to settle and while still hot filter into a 200 cc. graduated flask, washing thoroughly with hot water. Cool and make up to 200 cc.

Measure off 25 cc. of standard permanganate solution into a casserole, add 5 cc. of 1 : 1 H₂SO₄ and 150 cc. of hot water and run in the alkaline nitrite solution slowly from a burette until the color disappears.

On the basis of the formula K₂NaCo(NO₂)₆·H₂O, 1 cc. of tenth-normal permanganate is equivalent to 0.000785 g. K₂O. It has, however, been found to be more convenient to use a permanganate solution of such strength that 1 cc. is equivalent to 1 milligram of K₂O, which would be 0.1274 normal.

Sodium Cobaltinitrite Solution.—113 grams of cobalt acetate are dissolved in 400 cc. of 20 per cent. acetic acid. 220 grams of sodium nitrite are dissolved in 400 cc. of water. The two solutions are mixed, allowed to stand at the ordinary temperature for 24 hours, removing the nitric oxide formed by evacuation with a filter pump, and then filtered.

In order to test the method a stock solution was made by dissolving chemically pure K₂CO₃, MgSO₄ and Ca₃(PO₄)₂ in HCl and determining the K₂O by the platonic chloride method. 20 cc. of this solution gave the following amounts of K₂O in grams:

Calculated from K ₂ CO ₃ taken.	Found by platonic chloride method.
0.19856	0.1990
0.19856	0.1984

In testing the method 20 cc. of the stock solution were precipitated and the precipitate decomposed with 20 cc. of saturated Ba(OH)₂ solution, the filtrate made up to 250 cc. and 20 cc. taken for analysis. The titration was made by adding the permanganate from a burette after first making a preliminary titration to ascertain the approximate amount of permanganate required. This feature has been improved upon in the final procedure adopted. The following results were obtained:

K ₂ O present. Gram.	Tenth-normal KMnO ₄ , cc.	K ₂ O found. Gram.
0.015896	20.1	0.01578
0.015896	20.2	0.01586
0.015896	20.2	0.01586
0.015896	20.1	0.01578

Another determination was made using exactly the

¹ Jour. Chem. Soc., 77, 1076-80 (1900).

same method but with 30 cc. of $\text{Ba}(\text{OH})_2$ solution to determine the effect of an excess of alkali, with the following results:

K_2O present. Gram.	Tenth-normal KMnO_4 , cc.	K_2O found. Gram.
0.015896	20.1	0.01578
0.015896	20.1	0.01578

The effect of different amounts of NaOH used for the decomposition of the cobaltinitrite precipitate is shown by the following results. The method used was exactly the same as before, but 50 cc. of the alkaline nitrite solution were used for the titration.

With 25 cc. of five per cent. NaOH .		
K_2O present. Gram.	Tenth-normal KMnO_4 , cc.	K_2O found. Gram.
0.03974	41.6	0.03266
0.03974	41.8	0.03281
0.03974	41.8	0.03281
With 50 cc. of five per cent. NaOH .		
0.03974	48.4	0.03799
0.03974	48.4	0.03799
0.03974	48.4	0.03799
With 75 cc. of five per cent. NaOH .		
0.03974	52.8	0.04145
0.03974	52.9	0.04153
0.03974	52.9	0.04153

With still larger amounts of NaOH the cobalt was taken into solution to such an extent that the blue color was quite perceptible in the filtrate and no determinations were made. It is quite evident from the above results that NaOH is very unsuitable as a precipitant of the cobalt and its use was therefore abandoned.

In order to determine the ratio of N_2O_3 to K_2O in the cobaltinitrite precipitate a solution of 0.500 g. of K_2CO_3 in HCl was precipitated as before and the precipitate decomposed with $\text{Ba}(\text{OH})_2$. The filtrate was made up to 200 cc. and N_2O_3 and K_2O determined in 25 cc. portions by titration with tenth-normal permanganate and precipitation with platinic chloride with the following results:

K_2O in original solution.	K_2O found.	N_2O_3 found.	Ratio found.	Ratio theor.
0.04189	0.04285	0.1027	0.4173	0.4130

AGRICULTURAL EXPERIMENT STATION,
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TREATMENT OF CREAMERY SEWAGE BY THE SEPTIC TANK PROCESS.¹

By JAMES TEN BROECK BOWLES.²

Received January 20, 1911.

In the manufacture of butter and cheese there is a comparatively large amount of waste product, part of which can be returned to the farmer for stock-feeding, but a considerable amount cannot be so disposed of, and it is liable to create a nuisance when discharged into a stream or run upon land. That such a nuisance is created is shown by the following court decisions:

"The deposit of refuse from a creamery into the bed of a stream flowing through plaintiff's land and

near his buildings, polluting the water and giving off noxious gases affecting the use and enjoyment of the plaintiff's property, is a nuisance."

"A creamery company will be enjoined from causing offensive waste matter to flow upon another's pasture to its injury." (*Price vs. Oakfield Highland Creamery Co.*, 87 Wis., 536.)

The question of how creamery waste can be disposed of so as not to create a nuisance is therefore one of considerable importance, and although some work has been done on this subject in Europe and America the best method of treating such waste is a problem that still remains to be solved, and the following investigation was undertaken in the hope of throwing a little more light upon the subject.

Composition of Creamery Wastes.—Creamery waste consists of, pieces of cheese, butter, skim milk, whey, buttermilk, etc., diluted by washing from the floor, churns and pasteurizers. This mixture was found to be full of acid-producing bacteria which give the medium more or less acid reaction at first. After decomposition sets in and fermentation and putrefaction are well started, the medium gradually changes to a neutral rather than an acid one. It is plain to see that one is dealing with an undigested product, putrefaction not having yet started. In municipal sewage we have what is called a predigested product, that is, when the waste leaves the body it is full of putrefying bacteria, putrefaction and fermentation having already started. Thus when municipal sewage enters the septic tank decomposition has already set in and liquefaction goes on rapidly, while with creamery waste a long time elapses before putrefaction has even started.

The flow of creamery waste is not constant and for that reason is difficult to manage. In the mornings a large amount is received soon after churning, towards noon another large amount is received consisting largely of water used in cleaning up the floor where milk and cream are spilt. In the afternoon buttermilk and skim milk and washings are often turned into the tank.

Most of the cooling water has been cut off from the septic tank as the water is clean and there is no need of it going through the tank.

TABLE I.—CHEMICAL COMPOSITION OF CREAMERY SEWAGE FROM UNIVERSITY DAIRY AS COMPARED WITH OTHER CREAMERIES AND WITH MUNICIPAL SEWAGE.

	PARTS PER MILLION.			
	University dairy.	Elkhorn creamery.	Garnet creamery.	Madison City sewage.
Free ammonia.....	26.98	32.2	47.0	39.25
Alb. ammonia.....	38.55	43.8	105.5	6.0
Nitrates.....	0.0	0.0	0.0	0.0
Nitrites.....	0.0	0.0	0.0	0.0
Total solids.....	1702.8	2121.5	7575.0	896.4
Loss on ignition.....	169.3	1200.0	2216.0	201.0
Oxygen cons.....	396.2	311.6	261.0	79.6
Suspended matter.....	134.16	521.0	668.0	130.0
Putrescibility.....	7.9 hrs.	6 hrs.	4 hrs.	1/2 day

The free ammonia figures of the creamery sewage do not vary a great deal from those of the municipal sewage. The University Dairy sewage figures are much lower than those of the other creameries.

¹ This research work was carried on while Chemist of Wisconsin State Hygienic Laboratory, University of Wisconsin.

² Sanitary Chemist, Cristobal, Canal Zone.

In the albuminoid ammonia the University Dairy is still lower than the other creameries, but all of the creamery sewage is much higher in albuminoid ammonia than the municipal sewage.

The total solids and loss on ignition are much lower in the University Dairy sewage than in the other creameries, but are higher than in the municipal sewage.

The oxygen consumed figures, as well as the sus-

As noted in the description of the plant, the tank holds a day's flow and the dosing chambers hold about one-sixth of the amount of the tank. The tank would hold a little more if the dosing chambers were closed; thus, by dosing the tank six times per day, the sewage would remain one day in the tank. In Table III can be seen the results.

In comparing the total solids, nitrogen figures, oxygen consumed and putrescibility, it is found

TABLE II.—THE VARIABILITY OF CREAMERY SEWAGE AT UNIVERSITY DAIRY.

July, 1907.	PARTS PER MILLION.						Average
	17.	20.	22.	24.	26.	27.	
Free ammonia.....	34.4	25.0	26.0	29.0	24.3	23.2	26.98
Alb. ammonia.....	43.6	45.5	41.2	38.0	32.0	31.0	38.55
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total solids.....	3494.0	1208.0	1106.0	2201.0	1206.0	1202.0	1702.8
Loss on ignition.....	300.0	121.0	132.0	200.0	141.0	120.0	169.3
Oxygen consumed.....	227.2	600.0	425.0	465.0	410.0	250.0	396.2
Suspended matter.....	139.0	140.0	138.0	142.0	125.0	121.0	134.16
Putrescibility.....	8 hrs.	8.5 hrs.	8 hrs.	7.5 hrs.	6.5 hrs.	8.5 hrs.	7.9 hrs.

ended matter, are higher than in the municipal sewage.

All of the creamery sewages are more putrescible than the municipal sewage.

From this comparison it can be seen that creamery sewage is much higher in organic matter than municipal waste. The University Dairy sewage does not seem to be as concentrated a sewage as the other creameries' sewage.

In looking over Table II, one cannot find two sets of data that are very near alike. Creamery sewage is very hard to treat because it sometimes comes at

that the tank is not doing more than fifteen to sixteen per cent. purification. The effluent from the septic tank is much less putrescible than the raw sewage. When this effluent is turned out upon the beds a further purification is obtained in Table IV.

In dosing the septic tank three times per day it gives an improvement over that of dosing six times per day. This improvement is very slight and is noticed more in the putrescibility test than in any other place. The next greatest change is in the total solids and loss on ignition.

There seems to be a greater improvement in the

TABLE III.—COMPOSITION OF RAW SEWAGE AND EFFLUENT FROM SEPTIC TANK WHEN THE TANK IS EMPTIED SIX TIMES PER DAY.

July.	Raw sewage.							Effluent from septic tank.						
	17.	20.	22.	24.	26.	27.	Aver.	17.	20.	22.	24.	26.	27.	Aver.
Free ammonia.....	34.4	25.0	26.0	29.0	24.3	23.2	26.9	10.0	12.0	11.0	13.5	10.0	12.6	11.6
Alb. ammonia.....	43.6	45.5	41.2	38.0	32.0	31.0	38.5	15.6	35.0	20.5	36.0	18.9	33.0	26.5
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total solids.....	3494.0	1208.0	1106.0	2201.0	1206.0	1002.0	1702.0	1090.0	1850.0	1764.0	1541.0	1691.0	1521.0	1726.1
Loss on ignition.....	300.0	123.0	132.0	200.0	141.0	120.0	169.3	164.0	168.0	171.0	159.0	162.5	161.0	164.2
Oxygen consumed.....	227.2	600.0	425.0	465.0	410.0	250.2	396.2	137.0	140.0	135.0	143.0	130.0	128.0	135.8
Susp. matter.....	139.0	140.0	138.0	142.0	125.0	121.0	134.0	85.0	96.0	100.0	106.0	110.0	108.0	100.1
Putrescibility.....	8 hrs.	8.5 hrs.	8 hrs.	7 hrs.	6.5 hrs.	8.5 hrs.	7.9 hrs.	1/2 day	1/2 day	1 day	13 hrs.	12 hrs.	15 hrs.	13 hrs.

one time very dilute, then again very concentrated. In some instances the total figures are three or four times as great as in others.

The creamery sewage does not contain any nitrites or nitrates. In using the septic tank, the important

effluents from the sand beds than there is in the effluents from the septic tank. In the effluents from the sand bed the albuminoid ammonia has decreased and a trace of nitrites is found, showing that nitrification is going on.

TABLE IV.—COMPOSITION OF RAW SEWAGE AND EFFLUENT FROM SEPTIC TANK WHEN THE TANK IS BEING EMPTIED THREE TIMES PER DAY.

	Raw sewage.						Effluent from septic tank.					
	1.	8.	10.	12.	14.	Average.	1.	8.	10.	12.	14.	Average.
Free ammonia.....	20.0	27.0	21.0	8.5	13.0	16.9	30.0	28.0	32.0	32.0	27.0	29.8
Alb. ammonia.....	38.2	32.4	35.0	43.0	50.0	39.7	18.5	19.6	40.0	19.5	51.0	29.7
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total solids.....	1580.0	1468.0	1562.0	1660.0	2500.0	1754.0	1420.0	1310.0	1222.0	1460.0	1211.0	1324.6
Loss on ignition.....	740.0	692.0	685.0	700.0	570.0	677.4	150.0	148.0	152.0	150.0	160.0	150.0
Oxygen consumed.....	306.2	310.5	290.1	227.2	147.2	256.2	138.5	129.2	132.4	138.5	128.5	133.4
Suspended matter.....	128.0	130.0	125.0	180.0	130.2	101.5	128.0	126.0	100.0	120.0
Putrescibility.....	6 hrs.	5.5 hrs.	6 hrs.	7 hrs.	5 hrs.	5.9 hrs.	18 hrs.	17 hrs.	18 hrs.	18 hrs.	17 hrs.	17.6 hrs.

point to be considered is how long a time it is necessary for the sewage to remain in the tank in order to have it sufficiently decomposed.

In Table V, dosing tank twice per day, obtains an improvement over dosing three times per day. First, there is a decrease of albuminoid ammonia and an

increase of free ammonia figures, which shows that the organic compounds are breaking up and passing off as free ammonia and that less organic substances remain to break up and pass off as albuminoid ammonia.

The putrescibility point was higher in the last table than it was in the former, but the effluent is not yet good enough, and further investigation must be made.

In Table VI the septic tank has been dosed once per day and a great improvement is noticed. In this table the ammonia content is lower and the albuminoid ammonia figures are about half as high as formerly.

TABLE V.—RAW SEWAGE AND EFFLUENT FROM SEPTIC TANK WHEN THE TANK IS BEING EMPTIED TWICE PER DAY.

August.	PARTS PER MILLION. Raw sewage.				Effluent from septic tank.			
	16.	19.	23.	Aver.	16.	19.	23.	Aver.
Free ammonia.....	30.0	17.0	19.7	22.23	46.5	50.6	48.6	46.5
Alb. ammonia.....	47.5	56.0	62.0	55.1	26.25	29.2	30.1	28.85
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total solids.....	2580.0	3080.0	2890.0	2850.0	1430.0	1260.1	1360.2	...
Loss on ignition.....	570.0	1050.0	986.4	868.8	370.0	180.6	182.9	...
Oxygen consumed.....	147.2	390.0	416.0	317.7	239.2	182.9	179.3	...
Putrescibility.....	5 hrs.	4.5 hrs.	5 hrs.	4.8 hrs.	1 day	1 day	1 day	1 day

There are traces of nitrites and quite a little of nitrates. The total solids are lower and the putrescibility point a great deal higher. There is at least a reduction of sixty per cent. of solid matter. Taking the albuminoid ammonia figures, there is at least a reduction of two-thirds in organic matter; with respect to oxygen consumed figures there is a reduction of two-thirds in organic matter which is able to be oxidized.

effluents, dosing at periods from six times a day to once per week.

There is shown a gradual increase of free ammonia and a decrease of albuminoid ammonia. This is caused by the bacterial action upon the organic matter, the longer the sewage remains, the less albuminoid ammonia there is since it goes off as free ammonia after being decomposed. There is also an increase in the nitrites and nitrates, commencing with none at first. As to the solids, there is not much change until the dosing of the tank once per day is reached, then there is a general decrease. The same is true of the oxygen consumed figures. In the putrescibility test

there is not much difference between dosing once per day and dosing once every two and one-half days. The end point seems to be reached when dosing once per day. There is not enough change after that to pay to let it remain longer.

CONCLUSION.

From the study of creamery sewage disposal the

TABLE VI.—RAW SEWAGE AND EFFLUENT FROM THE SEPTIC TANK, WHEN THE TANK IS BEING EMPTIED ONCE PER DAY.
PARTS PER MILLION.

	Raw sewage.									
	Aug. 20.	Aug. 28.	Sept. 2.	Sept. 16.	Oct. 30.	Nov. 25.	Dec. 10.	Jan. 10.	March. 10.	
Free ammonia.....	19.7	13.0	10.4	25.0	15.0	20.0	15.0	12.0	10.0	
Alb. ammonia.....	62.0	50.0	53.1	45.5	25.1	30.0	30.0	30.0	28.5	
Nitrites.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Nitrates.....	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Total solids.....	2350.0	1666.0	1492.0	1202.0	1356.0	1000.0	1521.0	1421.0	1132.0	
Loss on ignition.....	1002.0	700.0	739.1	223.0	434.0	625.0	721.0	521.0	3334.0	
Oxygen consumed.....	451.2	227.2	245.0	340.0	292.0	248.5	361.0	282.0	195.0	
Suspended matter.....	
Putrescibility.....	5 hrs.	7 hrs.	7 hrs.	7.5 hrs.	6 hrs.	8 hrs.	9 hrs.	8.5 hrs.	6.5 hrs.	

	Effluent from septic tank.									
	Av.	Aug. 20.	Aug. 28.	Sept. 2.	Sept. 5.	Oct. 30.	Nov. 25.	Jan. 10.	Feb. 22.	Aver.
Free ammonia.....	15.5	36.2	35.4	43.0	40.3	60.0	50.4	40.2	36.0	42.6
Alb. ammonia.....	39.9	12.9	13.75	12.0	12.8	8.25	12.4	12.5	20.4	13.12
Nitrites.....	0.0	trace	trace	0.2	0.1	trace	0.05	0.09	trace
Nitrates.....	0.0	trace	0.5	0.09	0.10	0.60	0.7	1.0	0.895	0.385
Total solids.....	1482.2	1106.4	1008.5	980.2	890.0	984.0	865.0	721.0	628.0	897.98
Loss on ignition.....	588.78	149.3	152.4	102.0	99.0	105.0	141.0	102.0	110.0	120.08
Oxygen consumed.....	293.5	102.4	108.3	80.0	78.0	80.0	85.3	95.0	79.6	88.57
Suspended matter.....
Putrescibility.....	7.1 hrs.	1 day	1 day	1.5 days	1 day	1.25 day	1.25 day	1.5 day	1.5 day	1.25 days

Then with the nitrites and nitrates appearing, it is safe to say that with respect to the above figures, the tank will average sixty-five per cent. in reduction of organic matter when dosing once per day. The effluent has a putrescibility test of one and a half to two days when incubated at 37.5° C., which signifies a good effluent.

Table VII takes up the comparisons of the septic

following conclusions are obtained:

1. It has been shown that the septic tank, when the sewage remains in it six days, will liquefy and decompose the solid particles in the creamery sewage.

2. By allowing the sewage to remain in the tank six days gives a reduction of sixty to sixty-five per cent. of the organic matter.

3. This sewage must remain in the tank much longer than municipal sewage. There are many lactic acid organisms at work which keep the putrefactive organisms from growing. Just as soon as the lactic acid organisms have acted upon all the sugar these organisms will not be as active as formerly, and putrefactive bacteria will commence to grow.

4. When the sewage is allowed to remain in the tank six days, a stable effluent is obtained with no putrid odor.

5. If a creamery was so situated that it would be impossible to turn the effluent into a stream, then the effluent would have to be run on to a pasture or field near-by, or on to gravel beds. Care must be used in turning the effluent on to gravel beds as there is some

was shipped several hundred miles, some of it having been purchased in the open market, and irregularities in composition, as pointed out by them, may in part be due to differences in degree of ripeness at the time of gathering.

In 1904 Hume and Miller¹ published the results of a study of a number of varieties of pineapples grown in Florida, including several of the same varieties used by Munson and Tolman, and concluded from their studies that the acid content and total sugars in different varieties vary between wide extremes. These authors state that pineapples which ripen during the winter months contain less sugars than when ripening in summer; also, that usually the acidity varies inversely with the total sugars. Recently, Blair and

TABLE VII.—COMPARISON OF SEPTIC EFFLUENTS, DOSING FROM SIX TIMES PER DAY TO ONCE PER WEEK.

Dosing.	PARTS PER MILLION.					
	6 times per day.	3 times per day.	Twice per day.	Once per day.	Once every 2½ days.	Once per week.
Free ammonia.....	11.6	29.8	48.6	42.6	58.1	75.6
Alb. ammonia.....	26.5	29.7	30.1	13.12	1.5	1.25
Nitrites.....	0.0	0.0	0.0	1.0	2.0
Nitrates.....	0.0	0.0	0.0	0.385	0.0	0.0
Total solids.....	1726.1	1324.6	1360.2	897.98	325.0	195.0
Loss on ignition.....	164.2	150.0	182.9	120.08	115.0	85.0
Oxygen cons.....	135.8	133.4	179.3	88.57	18.0	17.0
Suspended matter.....	100.1
Putrescibility.....	13 hrs.	17.6 hrs.	1 day	1.80 day	2 days	3 days

liability of contaminating the creamery well water with the sewage. This has happened at Elkhorn, Wisconsin.

6. When a creamery has only a small septic tank, then filter beds should be used to further purify the effluent.

7. Cleaning of the septic tank and filter beds will depend upon the amount of flow, and should be attended to whenever the effluent deteriorates.

8. The results of this study answer the purpose of the investigation and show, first, the septic tank will dispose of creamery waste; second, it is a cheap method; third, it is applicable to both large and small creameries.

[CONTRIBUTION FROM THE LABORATORY OF THE HAWAII EXPERIMENT STATION, PAPER NO. 3.]

A STUDY OF THE COMPOSITION OF HAWAIIAN PINEAPPLES.

By W. P. KELLEY.

Received December 9, 1910.

In 1903 Munson and Tolman¹ concluded, from an extensive investigation of pineapples from Florida, Cuba, Porto Rico, Bahama and Singapore, that neither the variety nor the latitude in which the fruit was grown exercised any influence on its composition. The ratio of reducing sugars to sucrose in a given variety, however, was found to vary greatly. One pineapple of the Smooth Cayenne variety, for instance, was found to contain 3.17 per cent. reducing sugars and 7.51 per cent. sucrose, while another of the same variety contained 9.75 per cent. reducing sugars and only 2.98 per cent. sucrose. Some pineapples were also reported which contained abnormally small percentages of sugars. The fruit used by these authors

Wilson² made an extensive investigation of the composition of pineapples as affected by the use of fertilizers.

The pineapple soils of Hawaii³ have been derived from the disintegration of basaltic lava, and as regards both chemical and physical properties, are very unlike soils elsewhere that are devoted to pineapple culture. A study of the composition of pineapples from these soils is, therefore, not without interest. In addition, the chemical changes taking place during the process of development and ripening have also been investigated. The Smooth Cayenne is practically the only pineapple cultivated in these islands and hence the discussion in this paper relates to this variety only. In nearly every instance the pineapples were gathered by the writer, and were selected with special reference to securing representative fruit of uniform ripeness. Generally, except as otherwise noted, the analyses were made on the following day.

The methods employed in this work are essentially those given under the Official Methods for the Analysis of Fruits and Fruit Products.⁴ The solids in the juice were calculated from the specific gravity by use of the tables of H. Ellion, nitrogen was determined by the ordinary Kjeldahl method, reducing sugars by the volumetric Fehling solution method and sucrose by double polarization, the cane sugar being calculated from the formula $S = \frac{100(P - 1)}{142.66 - T}$. The total sugars

as invert were determined by digesting for two hours at the temperature of boiling water, 20 grams of the fruit in 200 cc. dilute hydrochloric acid, neutralizing, filtering and then determining the reducing power

¹ Florida Sta., Bull. 70, 59-61.

² *Ibid.*, 101.

³ THIS JOURNAL, 1, 533-8 (1909).

⁴ U. S. Dept. Agric., Bur. Chem., Bull. 107, 77-82 (revised).

¹ J. Am. Chem. Soc., 35, 272-80; U. S. Dept. Agric., Bur. Chem., Bull. 87.

of the filtrate by use of Fehling's solution. The acidity was determined by direct titration with $N/10$ KOH with the aid of phenolphthalein, and the results expressed as sulphuric acid. The chief acid of pineapples is citric but is here expressed as sulphuric.

Table I contains the results of the analyses of pineapples that thoroughly ripened in the field. These pineapples were taken from several districts in the

TABLE I.—THE COMPOSITION OF NORMALLY RIPENED PINEAPPLES.

Serial No.	Nitrogen. Per cent.	Acidity as H_2SO_4 . Per cent.	Sugars.			Polarization		
			Reducing. Per cent.	Sucrose. Per cent.	Total. Per cent.	Direct.	Invert.	Temperature °C.
101	..	0.56	3.94	7.97	11.91	6.4	-3.7	32.0
102	..	0.53	3.84	8.36	12.20	6.9	-3.7	31.5
103 ¹	..	0.31	5.14	4.01	9.15	2.3	-2.8	31.0
104 ¹	0.06	0.22	6.20	3.63	9.83	2.0	-2.6	32.3
105	0.09	0.43	5.10	7.54	12.64	5.8	-3.8	30.5
106	0.08	1.05	3.86	9.45	13.31	7.7	-4.3	31.4
107	0.09	1.16	4.18	8.40	12.58	7.1	-3.6	30.8
108	0.08	0.63	2.78	7.36	10.14	5.4	-4.0	30.0
109	0.09	0.75	3.56	8.12	11.68	6.3	-4.0	31.7
110	0.09	1.03	4.72	9.88	14.60	7.4	-5.1	32.3
111	0.07	0.86	5.18	10.05	15.23	8.0	-4.7	32.7
112	..	0.99	4.59	10.12	14.71	8.4	-4.4	32.3
113	..	1.06	3.50	8.47	11.97	6.6	-4.2	30.3
114	0.09	0.71	4.12	6.93	11.05	4.9	-3.9	31.4
115	0.07	0.82	3.14	7.15	10.29	5.3	-3.8	31.0
123	..	0.42	4.54	7.41	11.95	5.0	-4.5	29.2
140	..	0.45	4.35	6.08	10.43	4.2	-3.5	32.0
141	..	0.68	4.00	6.97	10.97	4.9	-4.0	30.0
142	..	0.63	4.87	6.47	11.34	3.9	-4.3	30.2
143	..	0.65	4.85	6.85	11.70	4.6	-4.2	28.6
144	..	0.61	5.55	6.03	11.58	4.0	-3.7	30.0
Av.	0.08	0.74	4.23	7.88	12.11			

islands, from soils of vastly different composition and growing under a wide range of rainfall. While not noted in the table a careful study of the pineapples from different sections has failed to reveal any great variation in the composition due to rainfall or soil. Individual pines from the same field, however, vary considerably, especially in regard to total sugars and acidity. In the main there is a fairly definite ratio between the reducing sugars and sucrose, this being usually about as 1 to 2. In the case of pineapples Nos. 103 and 104 the ratio is somewhat reversed, but this is probably due to the fact that each of these pines was slightly overripe at the time of gathering, and in the opinion of the author had begun to ferment. This would not only account for the partial inversion of the sucrose, but also for the abnormally low sugar content. By further reference to this table it may be seen that there is a considerable variation in the acidity and that the percentage of acidity is somewhat proportional to the total sugar content.

Table II contains the results of the analyses of green pineapples. These pines were fully grown but had not begun to ripen. Pineapples used in fresh fruit shipment to California are generally gathered at this stage of development. Some peculiarities in the composition merit our attention. The acidity is not above that of the ripe fruit. The fiber is low as are the solids in the juice. The total invert sugar which was determined in such a way as to hydrolyze any carbohydrates

¹ Not included in averages.

that it may be supposed could give rise to sugars in the process of ripening, shows that a green pineapple even though full grown does not contain substances in sufficient quantity to produce a normal sugar content. In other words the pineapple plant does not store up in its green fruit any considerable amount of reserve material which is later converted into sugar. In this connection repeated tests have revealed not more than a mere trace of starch or dextrin in the fruit at any stage of development. The slightly greater percentage of total invert sugar than of the

TABLE II.—THE COMPOSITION OF GREEN PINEAPPLES.

Serial No.	Acidity as H_2SO_4 . Per cent.	Fiber. ¹ Per cent.	Solids in juice. Per cent.	Sugars.			Polarization.		
				Reducing. Per cent.	Sucrose. Per cent.	Total by addition. Per cent.	Direct.	Invert.	Temp. °C.
127	0.48	..	7.32	3.57	1.96	5.53	1.0	-1.5	30.5
128	0.44	0.19	5.92	3.17	0.78	3.95	0.0	-1.0	30.4
131	0.30	0.16	..	3.36	0.87	4.23	5.07	4.0	-0.7
132	0.33	0.17	..	3.03	1.88	4.91	5.10	1.3	-1.1
145	0.39	..	7.44	3.33	3.14	6.47	8.02	2.5	-1.5
Av.	0.39	0.17	6.89	3.29	1.72	5.01	5.80		

combined sucrose and reducing sugars may possibly be due to the fact that it is very difficult by use of the method of cold maceration to rupture each cell in a sample of green pineapple; whereas, under the influence of boiling hydrochloric acid, all the sugars were brought into solution. The proportion of reducing sugars to sucrose is almost the reverse of that in the ripe fruit. The reducing sugars are present in almost as large quantity as in the ripe fruit, while the accumulation of sucrose had only fairly begun.

A number of pineapples gathered when green were held at the laboratory until thoroughly ripe. Table III contains the analyses of such pineapples. The

TABLE III.—THE COMPOSITION OF PINEAPPLES WHICH RIPENED AFTER BEING PICKED GREEN.

Serial No.	Acidity as H_2SO_4 . Per cent.	Fiber. Per cent.	Solids in juice. Per cent.	Sugars.			Polarization.		
				Reducing. Per cent.	Sucrose. Per cent.	Total by addition. Per cent.	Direct.	Invert.	Temp. °C.
133	0.53	0.20	..	1.48	3.92	5.40	5.32	2.4	-2.6
134	0.60	0.21	6.78	1.13	2.26	3.39	3.57	1.3	-1.6
135	0.55	0.21	6.04	1.19	3.17	4.36	4.75	2.0	-2.0
136	0.63	0.25	6.54	1.06	2.26	3.32	3.75	1.1	-1.8
146	0.49	..	5.30	1.33	2.06	3.39	..	1.1	-1.5
147	0.39	..	5.13	1.27	2.03	3.30	..	1.0	-1.6
148	0.39	..	4.99	1.37	1.10	2.47	..	0.0	-1.4
Av.	0.51	0.22	5.79	1.26	2.40	4.12 ¹	4.35		

data show that in the ripening of pineapples after having been severed from the plant, the only change of importance that takes place is the conversion of reducing sugars into sucrose. The ratio between these sugars is practically the reverse of that in the green fruit. A general softening of tissue, and liquefaction within the cells had taken place, with a simultaneous development of a more pleasing flavor, but the total sugar content had not been increased.

¹ The fiber was determined according to the usual method for fiber determination in feeds.

² Average of 133, 134, 135 and 136 only.

Table IV contains the analyses of pineapples when approximately one-fourth ripe. We note that there is a

TABLE IV.—THE COMPOSITION OF PINEAPPLES ABOUT ONE-FOURTH RIPE

Serial No.	Acidity as H_2SO_4 , Per cent.	Solids in juice, Per cent.	Sugars.			Polarization.		Temp. °C.
			Reducing, Per cent.	Sucrose, Per cent.	Total, Per cent.	Direct.	Invert.	
126	0.62	7.34	3.03	3.79	6.82	2.8	-2.0	32
129	0.59	7.86	2.53	3.34	5.87	2.2	-2.1	28.4
130	0.59	8.36	2.83	3.83	6.66	2.6	-2.3	29.4
149	0.72	9.20	2.77	5.89	8.66	4.5	-3.0	30.8
150	0.75	10.93	2.56	5.25	7.81	4.0	-2.7	30
Av.	0.65	8.68	2.74	4.42	7.16			

slight increase in acidity and also a considerable increase in sucrose as compared with the green fruit.

Table V shows the composition of pineapples when half ripe. When the fruit has attained this develop-

TABLE V.—THE COMPOSITION OF PINEAPPLES HALF RIPE.

Serial No.	Acidity as H_2SO_4 , Per cent.	Solids in juice, Per cent.	Sugars.			Polarization.		Temp. °C.
			Reducing, Per cent.	Sucrose, Per cent.	Total, Per cent.	Direct.	Invert.	
116	0.78	11.83	2.74	7.33	10.07	5.7	-3.6	31.8
117	0.67	10.36	2.61	6.70	9.31	5.0	-3.5	31.7
124	0.63	...	2.38	6.83	9.21	4.9	-3.8	30.5
125	0.54	...	4.16	6.09	10.25	5.0	-2.7	32.2
Av.	0.65	...	2.97	6.74	9.71			

ment fully three-quarters of its maximum sugar has been stored up.

SUMMARY.

The composition of Hawaiian pineapples varies considerably. The total sugar content on the one hand was found to vary from 9.15 per cent. to 15.23 per cent., while on the other there is a range in acidity of from 0.22 per cent. to 1.16 per cent. Generally, though not always, the acidity increases with an increase in sugars. The average composition of pineapples grown in Hawaii is about equal to that reported from other countries.

Green pineapples contain less acidity than the ripe fruit and also a small percentage of fiber, reducing sugar and sucrose. Dextrin and starch do not occur in important quantities in pineapples at any stage. The reducing sugars and sucrose stand in inverse ratio to that of the ripe fruit. In the ripening of pineapples gathered green, the most important chemical change that takes place is the conversion of reducing sugars into sucrose, but the total sugar content appears not to be increased.

The cells of green pineapples as seen under the high-power microscope contain a thickened layer on the cell walls, which renders it difficult to express the juice from the cells. In the ripening process this layer gradually becomes dissolved away until at maturity the cell walls are extremely thin and easily ruptured. With pineapples that are gathered green and allowed to ripen the thickened coat on the cell walls also becomes dissolved, thus apparently increas-

ing the juice in the fruit but without materially changing its concentration.

During the normal ripening of the pineapple a rapid accumulation of sugars and a slight increase in acidity takes place. When the fruit becomes approximately half ripe, it contains at least three-fourths of its maximum sugars.

THE DETERMINATIONS OF TOTAL SOLIDS IN MILK.¹

By PAUL POETSCHKE.

Received Feb. 24, 1911.

In the routine contamination of milk, the analysis is usually restricted to the determination of total solids, fat and specific gravity. Generally an examination for the more common preservatives is also included.

The object of the present article is to consider particularly the determination of total solids as accomplished by the aid of a special pipette devised for delivering five grams of milk of known specific gravity. Inasmuch as the specific gravity is essential to the proper use of this pipette some essential features relating to specific gravity will be considered.

Specific Gravity.—The New York Board of Health lactometer is the instrument usually employed in routine milk inspection. These instruments, as commonly constructed, require a comparatively large volume of milk, and if used for general laboratory work, would greatly inconvenience the inspector when many samples are taken for examination. Although many lactometers of reduced size are in use, it may be of interest to describe one of these forms,² which require but four ounces of milk. Fig. 1 is an exact representation of the instrument. A cylindrical jar (height 11.0 cm., diameter 4.3 cm.), made of brass tubing with a copper bottom soldered thereto, serves as a container for the milk. A sufficient quantity of the well-mixed sample, cooled to a few degrees below 60° F., is poured into the jar and stirred with a dairy thermometer until the temperature reaches 60° F. The lactometer is then carefully lowered into the jar, and when it becomes stationary, the reading recorded. Too much stress cannot be laid upon a proper standardization of the instrument. I have found lactometers to be incorrectly graduated in some cases to the extent of 4° to 5°. The simplest method of standardization is to compare the instrument in question with a standard lactometer. However, if such a standard is not at hand, a series of salt solutions are prepared and their specific gravity determined at 60° F. with a pycnometer, as in the following case, Table I:

TABLE I.

Specific gravity at 60° F., by pycnometer.	Corresponding lactometer	Observed reading on instruments (Standard)	
		One.	Two
1.0245	84.5°	84.0°	84.0°
1.0278	96.0	96.0	96.0
1.0312	107.0	107.0	107.0

¹ Read before N. Y. Section Am. Chem. Soc., Feb. 10, 1911.² Devised some years ago by Dr. Deghué, of this laboratory.

Having thus verified the standard, we can proceed to standardize other instruments by comparison, which is much simpler, since it is not necessary to standardize at 60° F. The comparison can be made at any other temperature, as long as the temperature of the solution remains uniform while the instrument in question is compared with the standard. Table II gives the result of comparison of several instruments with the standard:

TABLE II.

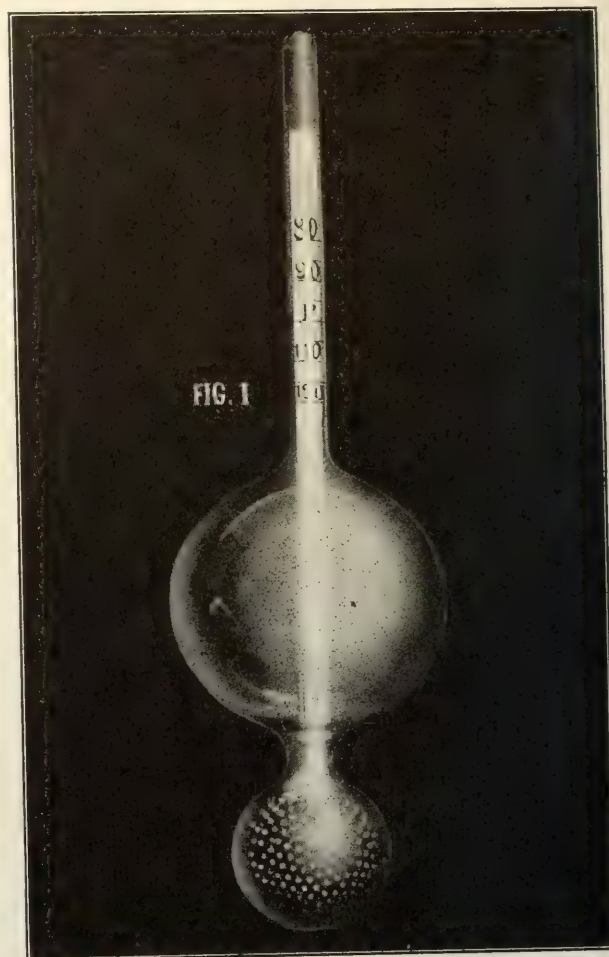
Lactometer number.	Reading on Standard lactometer.	Observed reading on lactometer.	Correction.
3	82	86	-4°
	95	98	-3
	108	110	-2
	117	118	-1
4	82	86	-4
	94	98	-4
	107	108	-1
	116	117	-1
5	81	85	-4
	94	97	-3
	106	108	-2
	116	117	-1
6	87	86	+1
	94	92	+2
	107	104	+3
	118	114	+4
7	83	82	+1
	91	89	+2
	112	100	+2
	114	111	+3

The observed corrections noted in Table II are plotted on cross-section paper to facilitate ready reference and avoid errors in interpretation. If the lactometer reading of a sample of milk is taken at any temperature other than 60° F., a correction of one degree is necessary for a difference of 2° F. Of course, a corresponding amount is added if the temperature is above 60° F., and subtracted if below 60° F.

Total Solids.—The usual method of determining total solids is to introduce five grams of milk into a weighed flat-bottomed dish. After the dish has been weighed, a five-gram weight is added to those already on the balance pan, and five cc. of the thoroughly mixed sample drawn into a dry five cc. pipette. This is emptied into the dish until counterbalanced by the weights, which is readily accomplished. By this means five grams are weighed quicker than if a full five cc. were delivered and weighed, and this procedure has the further advantage of shortening the final calculation. The dish is then placed in the water bath, until nearly all of the water is evaporated, and finally dried to constant weight at 100° C. Provided the temperature is constantly maintained at 100° C., a practically constant weight is obtained in 2½ hours. A thermoregulator,¹ very convenient for controlling the temperature, has been described by the author.

To reduce as much as possible the time required for all routine determinations, is an object worthy of consideration in the laboratory where many similar determinations are carried out. However, any shortening of an accepted or reliable process must not

noticeably affect its accuracy. The author has devised a pipette graduated so as to deliver five grams of milk of known specific gravity, which for convenience is graduated in degrees of the N. Y. Board of



Health lactometer. Although graduated in this manner, the equivalent specific gravity and Quevenne lactometer degrees can be interchanged according to Table III, which also gives the weight of water, corresponding in volume to five grams of milk at 60° F.

Repeated trials of pipettes of varying dimensions were made until one of satisfactory form was secured. The body of the pipette is not of much significance, but the suction tube and calibrated delivery tube must be of such internal diameter as to allow of accurate measurement and fairly uniform time of delivery. The pipette is shown (¼ actual size) in Fig. 3. The internal diameter of the calibrated tube is 1.0 mm. and of the suction tube 2.5 mm. The temperature of the milk is preferably adjusted to 60° F., well mixed and drawn into the pipette until the zero mark coincides with the lower meniscus. It is then allowed to drain into the weighed dish, by touching the side of the dish with the tip of the pipette, until the mark corresponding to the lactometer reading of the milk is reached. Ordinarily the sample for the total solids determination is taken directly after the lactometer reading is recorded so as to obviate

¹ J. Am. Chem. Soc., 31, 1218.

TABLE III.

Specific gravity, 60° F.	N. Y. Board of Health.	Quevenne scale.	Weight of water corresponding in volume to five grams of milk at 60° F.
1.0203	70°	20.3	4.9005
1.0206	71	20.6	4.8991
1.0209	72	20.9	4.8976
1.0212	73	21.2	4.8962
1.0215	74	21.5	4.8948
1.0217	75	21.7	4.8938
1.0220	76	22.0	4.8924
1.0223	77	22.3	4.8909
1.0226	78	22.6	4.8895
1.0229	79	22.9	4.8881
1.0232	80	23.2	4.8866
1.0235	81	23.5	4.8852
1.0238	82	23.8	4.8838
1.0241	83	24.1	4.8823
1.0244	84	24.4	4.8809
1.0246	85	24.6	4.8799
1.0249	86	24.9	4.8785
1.0252	87	25.2	4.8771
1.0255	88	25.5	4.8757
1.0258	89	25.8	4.8742
1.0261	90	26.1	4.8728
1.0264	91	26.4	4.8714
1.0267	92	26.7	4.8700
1.0270	93	27.0	4.8686
1.0273	94	27.3	4.8671
1.0275	95	27.5	4.8661
1.0278	96	27.8	4.8648
1.0281	97	28.1	4.8633
1.0284	98	28.4	4.8619
1.0287	99	28.7	4.8605
1.0290	100	29.0	4.8591
1.0293	101	29.3	4.8577
1.0296	102	29.6	4.8563
1.0299	103	29.9	4.8549
1.0302	104	30.2	4.8534
1.0304	105	30.4	4.8525
1.0307	106	30.7	4.8511
1.0310	107	31.0	4.8497
1.0313	108	31.3	4.8482
1.0316	109	31.6	4.8468
1.0319	110	31.9	4.8454
1.0322	111	32.2	4.8440
1.0325	112	32.5	4.8426
1.0328	113	32.8	4.8412
1.0331	114	33.1	4.8398
1.0333	115	33.3	4.8388
1.0336	116	33.6	4.8374
1.0339	117	33.9	4.8361
1.0342	118	34.2	4.8347
1.0345	119	34.5	4.8333
1.0348	120	34.8	4.8319
1.0351	121	35.1	4.8305
1.0354	122	35.4	4.8290
1.0357	123	35.7	4.8276
1.0360	124	36.0	4.8262
1.0362	125	36.2	4.8253
1.0365	126	36.5	4.8239
1.0368	127	36.8	4.8225
1.0371	128	37.1	4.8211
1.0374	129	37.4	4.8198
1.0377	130	37.7	4.8184

total solids, proteids and fat. First of all, the sample must be uniform and reasonably fresh, since if it is partly churned or sour a reliable result cannot be obtained. Such milk requires preliminary treatment in order to secure a proper sample for any determination whatsoever. With slightly churned milk, the sample is warmed so as to melt the particles of but-

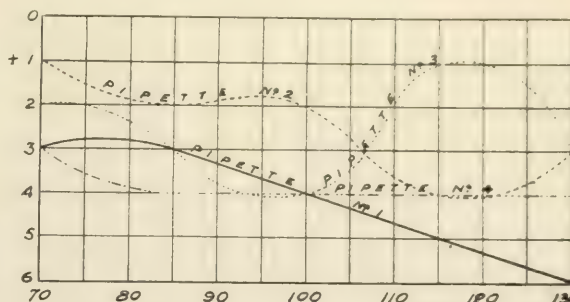


Fig. 2.

ter and shaken until a uniform mixture is obtained. In the case of sour milk it becomes necessary to treat the sample with a small quantity of alkali, preferably ammonium hydroxide, which dissolves the coagulated casein. Any sample which requires such treatment should not be measured by means of the pipette for the total solids determination. The largest source of error is due to the variable retention of different milks, but the time of delivery (average 100 seconds) is sufficiently great to reduce the retention to a min-

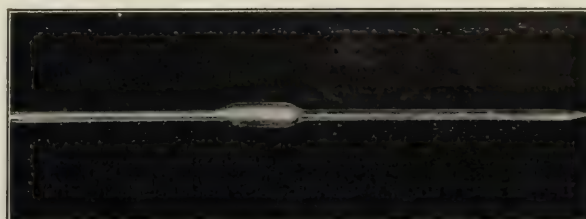


Fig. 3.

imum. Table IV shows the amount of retention for various samples and the influence on the total solids determination. The amount retained was obtained by delivery to the requisite mark on the pipette into a stoppered weighed tube:

TABLE IV.

Sample number.	Lactometer reading at 60° F.	Weight delivered corresponding to lactometer.	Retention in grams.	Total solids corrected for retention.	Total solids assuming five grams to have been delivered.
1	113	4.9985	0.0015	12.06	12.06
2	110	4.9974	0.0026	12.28	12.27
3	115	4.9945	0.0055	12.39	12.38
4	117	4.9957	0.0043	12.73	12.72
5	82	4.9976	0.0024	9.25	9.25
6	90	4.9966	0.0034	9.82	9.81
7	113	4.9911	0.0089	12.34	12.32
8	114	4.9875	0.0125	12.37	12.33
9	114	4.9860	0.0140	12.39	12.35
10	113	4.9906	0.0090	12.34	12.32
11	113	4.9917	0.0083	12.33	12.32

From the results obtained the minimum retention was 0.0015 gram, the maximum 0.0140 gram, and

the necessity of again adjusting the milk to the proper temperature. The pipette is of still greater advantage when a complete analysis is required, as in the case of human milk. For instance, in the determination of total proteids by the Kjeldahl method five grams of the milk are delivered directly into the digestion flask without any weighing whatever. The same is true in the case of the fat determination by the Adams' paper coil method.

We now come to a consideration of the various factors which influence a correct delivery of five grams of milk, although it will be shown that these errors have little significance in an actual determination of

the average solid present. Assuming an average total weight of 10 cc per cent, the maximum error from this source is 0.02 per cent, and the average 0.01 per cent, which is well within the ordinary limits of accuracy.

Pipettes delivered by the makers require no be standardized. This is accomplished by delivering freshly boiled and cooled distilled water at 60° F. to the 10, 15, 20, 25 and 50 marks and weighing the water in a stoppered weighing tube. Table V gives the results of a calibration of four pipettes and the required corrections.

TABLE V

	Pipette 1	Pipette 2	Pipette 3	Pipette 4
Volume water at 60° F. de- livered as 10 mark	4.9995	4.9994	4.9995	4.9994
Equivalent increment	97"	96"	98"	97"
Correction	+0.01	+0.01	+0.01	+0.01
Volume water at 60° F. de- livered as 15 mark	4.4996	4.4993	4.4994	4.4991
Equivalent increment	97"	96"	97"	96"
Correction	+0	+0.01	+0.01	+0.01
Volume water at 60° F. de- livered as 20 mark	4.9996	4.9995	4.9994	4.9993
Equivalent increment	96"	96"	96"	96"
Correction	+0	+0.01	+0.01	+0.01
Volume water at 60° F. de- livered as 25 mark	4.9995	4.9994	4.9993	4.9992
Equivalent increment	96"	96"	96"	96"
Correction	+0.01	+0.01	+0.01	+0.01
Volume water at 60° F. de- livered as 50 mark	4.9994	4.9993	4.9992	4.9991
Equivalent increment	96"	96"	96"	96"
Correction	+0.01	+0.01	+0.01	+0.01

In order to simplify interpretations the corrections noted in Table V are plotted as in Fig. 1.

Table VI gives the result of total solids determinations made with the use of the pipette and in the ordinary manner.

TABLE VI

Sample number	Laboratory reading at 60° F.	Factor per cent.	Total solids	
			By the pipette Per cent.	By direct weighing Per cent.
10749	1.8	1.4	12.55	12.87
10750	1.8	1.6	12.32	12.39
10751	1.8	1.6	12.30	12.28
10754	1.8	1.4	11.42	11.49
10757	1.8	1.5	11.79	11.83
10759	1.1	4.5	18.21	18.28
10760	1.8	1.6	11.99	11.94
10761	1.8	1.4	11.80	11.89
10762	1.1	3.7	12.84	12.97
10767	1.1	3.7	12.84	12.41
10768	1.8	1.4	11.55	11.84
10769	1.1	3.4	12.86	12.86
10770	1.1	1.1	12.16	12.29
10771	1.8	1.6	12.24	12.26
10772	1.8	1.4	11.55	11.64
10781	1.8	1.4	12.32	12.30
10783	1.8	1.2	12.90	11.88
10785	1.15	3.5	12.55	12.49
10786	1.8	1.4	11.55	11.64
10787	1.8	1.4	11.80	11.95
10788	1.8	1.4	11.84	11.93
10789	1.8	1.7	12.29	12.34
10790	1.8	3.7	11.28	10.28

In 31 additional determinations, omitted for lack of space, the average variation by pipette and direct weighing was ± 0.04 per cent.

It is apparent that the results show good agreement, and considering the time and labor saved, I feel justified in describing the instrument. Mr. Gottlieb Greiner, of 40 John Street, New York City, has undertaken to make this pipette at a reasonable cost. I wish to acknowledge my indebtedness to my assistants, Messrs. J. Schreff, J. F. Kahrs, and E. S. Liebscher, for their assistance in the analytical work.

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PLANTS AND MACHINERY.

FILTRATION OF WATER.

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For a great many years the streams flowing through the more densely populated portions of our country have been subjected to a steadily increasing contamination. In spite of the various commissions, boards of health, prohibitive statutes and other attempts to regulate the condition the last ten years has seen a retrogression in the purity of surface waters that is most startling. Occasionally a very active commonwealth may deal with certain individual sources of contamination with a heavy hand, but instead of these attempts being received with acclamation their authors have been excoriated as people who are attempting to prevent the normal growth of the country by the repression of its industries.

The occasional sewage disposal plant met with or the perfunctory attempts of the manufacturers to disguise the unpleasant features of their waste liquors have had little result on the general flow. So discouraged are sanitarians and others becoming that they no longer demand that such streams shall retain their original purity, but are willing to compromise the entire matter by simply requiring that the contaminations shall not make a nuisance of the stream itself, that is, that all forms of matter may be emptied into it provided these forms are not of a sufficiently putrefactive nature to make the stream offensive. Of course certain chemical wastes, if discharged into the stream, would cause manufacturers below to protest and perhaps bring suit to stop their discharge, but this form of litigation is never of a satisfactory nature and is always enormously expensive. As a matter of fact the average manufacturer is placed between the devil and the deep sea. Above him is the in-

considerate manufacturer who persists in defiling the stream, and below him is the obdurate and unreasonable factory owner who objects to his industrial wastes. It is really remarkable the way a man's point of view can change merely by looking up or down stream. Everything that comes from above seems to be of a pernicious nature while everything discharged below seems perfectly harmless.

While the nature and degree of contamination may vary greatly in different streams, due to the population, nature of the industries upon its banks and proportion of pollution to the normal flow, the general contamination consists of sewage, paper mill wastes, waste dye liquors from wool, cotton and silk industries, waste from wool washeries, bleacheries, possibly a chemical factory waste and occasional spent tannery liquors. Nearly always will we also find profuse growths of organisms of a low type, particularly beggiatoa, which will frequently be seen in such enormous quantities as to interfere with the

acid it can be handled in a purifying plant. The strawboard factory waste, if sufficiently diluted, presents no serious problem but as a rule these factories are located on small streams and the strongly alkaline waste makes the general flow of the stream very alkaline indeed. The neutralization of this alkali, if it exists in large quantities, is an expensive and unsatisfactory process. The beet sugar waste is now being utilized by manufacturers of beet sugar so that this form of contamination fortunately has practically disappeared. The starch factories also have recently evolved a manner of treating their waste which we are led to believe is more than self-sustaining, so that both of these industries can be relied upon to eliminate what is now a source of infrequent but serious trouble.

These uncommon forms of contamination are, many of them, being eliminated by reason of the fact that the waste products can be utilized. The remainder are usually located in territories quite remote



Fig. 1. Settling basin for highly polluted water. Frame chemical feed house at right and brick filter houses at end of basin

flow of the stream. Then there are uncommon forms of contamination such as the waste liquor from sulphite pulp mills, strawboard factories, beet sugar waste, starch factory waste, etc. All of these represent a very serious form of contamination and which, if they exist in very considerable proportions, are bound to make the work of purification extremely difficult. The first-named, the sulphite waste, is an acid substance which interferes with the bacterial purification of the stream and must be neutralized with some alkaline substance before it can be purified. If it is not present in sufficient quantities to make the water

from cities so that they do not enter into the problem usually presented and as outlined in the forepart of this article.

While the various industries are the principal sufferers from stream contamination, they are also the principal contributors toward it. They must have water in large quantities and they must be provided with an outlet for their wastes. Moreover, certain conditions, such as labor, propinquity of the markets, availability of material, etc., demand that these industries shall be located in or near populated districts. Thus they are prevented from going to remote places

to procure a pure water and they are compelled to use the contaminated supplies invariably found in populated districts. The water supplied by municipalities and water companies ranges in cost from four cents to thirty cents per thousand gallons and such industries as paper mills, bleacheries, silk works, etc., use millions of gallons of water per day. To pay any such tremendous price for water would reduce their profits to nothing. Their very existence depends upon their ability to make the contaminated waters suitable for their requirements, and this problem, while apparently very complex, resolves itself in almost every instance into a comparatively simple one. The solution consists in the treatment of the polluted water with certain chemicals which will produce complete precipitation of the dyes, coagulation of the finer particles of suspended matter, and at least a partial oxidization of the sewage. After the chemical treatment a reasonable period of time to allow for sedimentation and completion of the chemical reactions must take place, after which the water is passed

must have a water that is crystal clear and absolutely colorless. For bleaching cotton a degree of purification not quite so thorough is required while for paper-making it is simply necessary to remove all of the suspended matter and those dyes which would have a tendency to discolor cellulose. The degree of purification attained depends very largely upon the preliminary treatment, or in other words, upon the amount and character of the chemicals employed to exhaust the colors, produce coagulation and oxidize the sewage.

No filter, of course, can remove dissolved substances from water in any appreciable quantity, and to effect a complete removal of many of the most annoying substances which are in solution or so finely divided that they cannot readily be retained by the filter, preliminary treatment should be resorted to. Simple coagulation, however, is only one of its offices.

Preliminary treatment in its broadest sense consists first in the addition of coagulants to exhaust the dyes and to gather together the finely divided particles

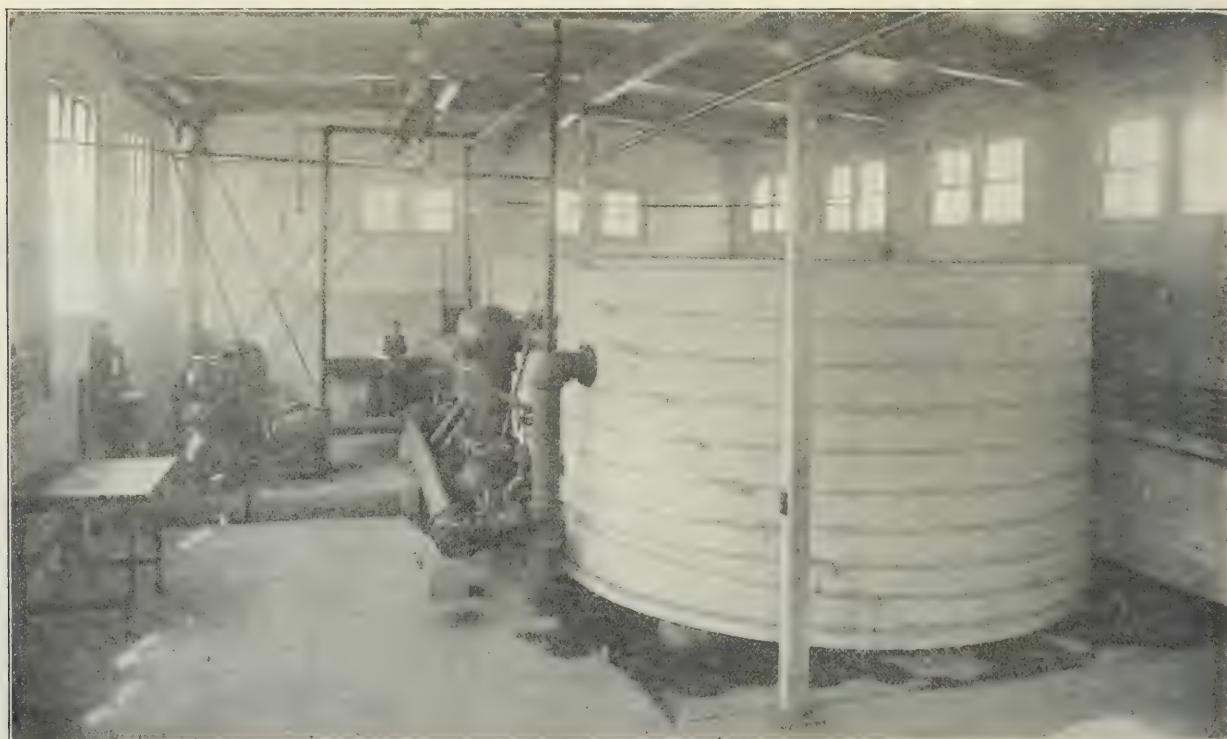


Fig. 2. Filter house: capacity, $2\frac{1}{2}$ million gallons.

through a filter plant of the so-called mechanical type, that is, a filter which can be washed in a few minutes by reversing the flow of water through it. This treatment must be effected in such a manner that the applied chemicals will not leave residual substances prohibitive to the use of the water.

Some industries require a very high degree of purification while others simply require the removal of suspended matter. Silk dye works undoubtedly require the highest degree of purification while cotton bleacheries, cotton and wool dye houses and paper mills come next in the order named. The silk dyer, on account of the extremely delicate shades demanded and the properties of the chemicals employed by him

of matter; the addition of some oxidizing agent to reduce the sewage to an innocuous form, and sedimentation to effect as large a removal of the precipitated matter as is possible before delivering the water to the filters.

The most reliable coagulant that can be used is sulphate of alumina. Other substances have been tried, many of them successfully, but for general efficiency and economy the sulphate of alumina is undoubtedly superior to any other substance. Sulphate of iron followed by lime has been used very extensively but in many cases plants using these substances have reverted to the aluminum sulphate.

Before sulphate of alumina is applied to a water an

analysis, of course, is necessary. Should the water be found to possess no alkalinity it must first be artificially produced, ordinary soda-ash or even building lime being perfectly applicable to this condition. The sulphate of alumina is applied in the form of a solution to the incoming water as it enters the settling basin. It is applied in quantities varying with the degree of pollution, and will range from one to as high as six grains per gallon in extreme cases with an average requirement for polluted waters of two and one-half grains to the gallon.

The chemical action of the sulphate of alumina is very rapid indeed. It almost instantly combines with the alkaline substances in the water to form hydrate of alumina. It also has a direct action upon almost every dye that is found in the stream, and it has a tendency to completely precipitate these dyes when mingled with each other. This effect is sometimes quite surprising because it frequently happens that pure solutions of the dyes themselves which are hardly effected by the sulphate of alumina will, when mingled with the various substances found in the stream, combine to form a general impurity which is quite amenable to treatment by the aluminum sulphate; that is to say, the dyes, mordants, etc., which are used in a dye house and which are not individually susceptible to alum treatment will, when mingled together and in conjunction with the lime existing in the water, the sewage and other industrial waste, form a highly discolored substance which can be completely precipitated by the sulphate of alumina.

In the actual preliminary treatment of the water, the matters precipitated have a tendency to gather together in flocculent masses quite visible to the naked eye. As a rule these substances tend to settle with considerable rapidity so that in three hours' time we find that the water has been rendered passably clear. If sewage, however, is present in any considerable quantity there is a tremendous growth of various forms of bacterial life, some of which possess the property of giving off gases in greater quantity than can be dissolved by the water itself. In fact, the solution of these gases in the water is not a condition to be desired, as many of them have a highly offensive odor. The worst condition of all, however, is the tendency of small bubbles of the gases generated to attach themselves to the matter which has settled and buoy it to the surface, thus preventing the most important action of all—sedimentation. Moreover, in the depth of the sludge the gases of decomposition are generated with such energy that masses several square yards in extent are sometimes brought to the surface where they break up and fall slowly to the bottom again. This process taking place over the entire surface of the settling basin destroys the benefits received from sedimentation, and during warm weather it would be quite possible for the settled water to leave the settling basin in worse condition than it entered.

Furthermore, the liquefying bacteria are also very active under the especially favorable conditions for their growth which exist within the settling basin

and much of the matter that has been precipitated, or in fact that had not been in a liquid form at all, is reduced to a solution through their offices. This action liberates the coloring matter which had been precipitated and the effluent from the filter will show these colors.

Of course, from the manufacturer's standpoint, the removal of the bacteria from the water is something that does not interest him. As a matter of fact, however, his water must be sterile or very nearly sterile to be properly purified as it is quite apparent that the bacteria can completely arrest the purification process. Moreover, if they are not destroyed they will grow in the underdrains of the filters, and even in the piping system throughout the factory, to such an extent as to obstruct the flow of water, so that it is quite apparent that some extremely powerful bactericide must be employed.

By reason of their efficiency and economy there are two substances which immediately present themselves, one calcium hypochlorite and the other sulphate of copper. Of the two, the calcium hypochlorite is far the more preferable, and in fact, copper sulphate is seldom used except in those cases where algae are troublesome. The calcium hypochlorite when used in quantities ranging from 1-5 parts per million not only destroys all of the bacteria that could make any trouble but it also tends to break up the sewage and to decompose many dissolved substances that might by future putrefaction cause great trouble with the water. This substance accurately applied produces the most wonderful results in the settling basins, and a water which possesses a high degree of color, a very offensive smell and much suspended matter will, after three hours' preliminary treatment in the settling basin, with the addition of the requisite quantities of alumina and hypochlorite, flow to the filters very largely clarified, with much of the color, a great deal of the suspended matter and almost all of the odor taken away. In other words, the water has been reduced to a filterable condition, and after passing through the filters it will be as bright, clear, sparkling and odorless as spring water.

These problems of purification are not to be approached without due consideration and a very careful study of the forms of contamination. There may be extraordinary forms of pollution that require some special form of treatment in addition to the usual chemical treatment in the ordinary rectangular settling basin. The presence of very large quantities of sewage makes a problem, which would otherwise be quite simple, very hard to handle. If the sewage contained is very high indeed recourse will have to be made to some of the standard methods of sewage disposal. In such cases possibly the most effective of all would be the Imhoff tank, but even if this were used it would have to be followed by chemical treatment in the usual settling basin.

A very important part of the preliminary apparatus is the chemical feed. It is necessary in almost all instances to apply the coagulants, oxidizing agents, etc., in a very exact manner. The chemical feed to

do this must be an apparatus which is capable of measuring the incoming water and applying to it the exact amount of chemicals required, proportionate to this flow. It often happens that the influx may vary from ten to ninety per cent. and the chemical feed must meet these changes rapidly and accurately. If not enough chemicals are applied the preliminary treatment is a failure. If an overdose of chemicals is applied the water cannot be used, so it is quite evident that this small and apparently insignificant apparatus is of great importance.

The proportion of chemicals required is best determined by means of some simple chemical test that can be conducted by operatives having no chemical knowledge. With regard to the amount of sulphate of alumina required the writer finds that any person of ordinary intelligence can determine the alkalinity of the water by means of *N/50* sulphuric acid, taking 100 cc. of the water to be tested and using erythrosine as an indicator. By conducting the test in the manner above described, each tenth of a cc. of acid consumed in titrating indicates an alkalinity of one part per million, and each grain of sulphate of alumina per gallon applied to the water reduces the alkalinity eight parts per million.

The sulphate of alumina solution is made up of standard strength in wooden tanks, one tank being prepared while the other is in use. Of course, the amount of alum used can always be determined by reference to the chemical feed, but the determination of the alkalinity at weekly intervals makes a very good check upon the laborer who usually attends to the preparation of the alum solution.

The soda solution where required is also made up in the same manner and the test conducted in the same manner. The hypochlorite of lime is made of standard strength in a separate tank with an agitator operated by hand. After it has settled clear the supernatant liquor is drawn into a solution tank from which it is taken by the chemical feed as required. As the quantity of this material used is so small the only test required with this is to make sure that there is no excess of hypochlorite, and so a solution of starch and potassium iodide is used as a qualitative test. If there is any indication of a blue color there is a very great excess of calcium hypochlorite being used and the feed should be very much reduced.

This method of dealing with the situation may not appeal to a chemist but there are many instances in industrial plants where very nice chemical determinations are conducted quite ignorantly but very successfully by people who have no chemical knowledge of what they are about. Where a chemist is employed by the works a more accurate determination can be made at suitable intervals, but the amount of calcium hypochlorite required is so far below that which can actually be consumed by the impurities in the water that an excess could only come from the grossest carelessness imaginable.

After the preliminary treatment of the water is completed the water passes through the filters, which are the most important and by far the most interesting part of the whole apparatus.

These filters must be constructed so that they will remove all suspended matter from the water and can be readily cleaned in a very few minutes' time. They must be capable of handling very large quantities of water, must occupy little space and be so constructed that there is no deterioration of the filtered water as they grow old. This means that the filter beds must wash perfectly every time the current is reversed and that there shall be no permanent concretions of the retained matter. They must also be capable of passing the water through them with a very slight loss of pressure, and economy of operation, next to efficiency, must be a distinguishing characteristic.

Following are the results of filtration upon badly polluted waters:

No. 1.—SAMPLE OF WATER FROM PASSAIC RIVER BELOW PATERSON, N. J.

	Color.	Turbidity.	Alkalinity.	Odor.
			Parts per million.	
Before filtration	deep bluish black	80	23	Musty
After filtration	colorless	0	7	Faint
Coagulant used	2 grains of sulphate of alumina per gallon.			
Sedimentation	2 hours, 15 minutes			

No. 2.—SAMPLE OF WATER FROM DUNDEE CANAL AT PASSAIC, N. J.

	Color.	Turbidity.	Alkalinity.	Oxygen	Bacteria
			Parts per million.	consumed.	per cc.
Before filtration	black	100	23	16.57	8,000
After filtration	colorless	0	3.6	1.83	40
Coagulant used	2½ grains of sulphate of alumina per gallon				
Sedimentation	about two hours				
Calcium hypochlorite	1 part per million				

No. 3.—SAMPLE OF WATER FROM DAN RIVER AT DANVILLE, VA.

	Color.	Turbidity.	Alkalinity.
	Hazen scale.		Parts per million.
Before filtration	50	4000	12
After filtration	0	5	10
Coagulant used	1 grain sulphate of alumina per gallon and carbonate of soda to neutralize it		
Sedimentation	¾ hour		

The so-called mechanical filter fulfils the above requirements. Unfortunately, this filter is supposed to have been evolved from the older type of slow sand filter, whose action depends principally upon a layer or film of impurities directly upon the surface of the sand. This slow sand filter is capable under average conditions of handling about three million gallons of water per acre per day and when properly taken care of shows a very high bacterial efficiency, but it does not possess a great bacterial efficiency immediately after cleaning or until the surface film gets thick enough to act as a strainer. Also when the rate of three million gallons per acre per day is exceeded materially there are short periods that occur during which the bacteria in the filtered water mount upward to an astonishing degree. Careful investigation have developed the fact that this surface film breaks in places, permitting the water to rush through the sand at those places at a high rate of speed, carrying all manner of impurities through with it. The best way of avoiding this trouble seems to be to keep the rate of filtration below three million gallons per acre per day.

The first successful mechanical filter was developed a good many years after slow sand filtration had been

come an assured success, and almost coincident with the perfection of this apparatus it was discovered that by the use of alum in the filtration process a very brilliant water could be delivered from the filters. The inventor, with a full knowledge of the theory of slow sand filtration, assumed that the hydrate of alumina formed by the addition of the alum made his surface layer much tougher and permitted a rate of filtration ranging from sixty to one hundred and twenty million gallons per acre per day. This belief in a tenacious surface layer has unfortunately been very largely adhered to by filter manufacturers, but the writer is firmly convinced that this theory is altogether erroneous. In the first place, the hydrate of alumina does not toughen the surface layer. If a water containing nothing but hydrate of alumina is applied to a filter so that it will form a surface layer, a rate of sixty million gallons per acre per day cannot be maintained without serious breaking through, the hydrate of alumina being so unstable that it cannot form a layer of reliable integrity. In the second place a surface layer with fine enough pores in it to retain the bacteria, which range from one twelve-thousandth to one twenty-five-thousandth of an inch on their longest dimensions, and the particles of fine argillaceous matter that give the water an opalescent tint—computed to be about $\frac{1}{100,000}$ of an inch in diameter—could not be forced even under very high pressure to let the water through at anything like the high rate of filtration that the mechanical filter does maintain successfully with only a slight loss of head. Still again we have seen that a surface layer on the slow sand filter breaks through readily at the very slow rate of three million gallons per acre per day, and there is no reason to believe that the mechanical filter acts differently.

With these points in view it must be apparent to every one that the surface layer is not the effective filter, but that some other process beside mere straining is responsible for the high efficiency of the mechanical filter.

A mechanical filter, in spite of its high rate of speed, is constructed of coarser sand of a much more uniform size than that used in the slow sand filter. While there is considerable latitude permissible in the size of the grains in different filters, an average grade of sand which gives interstitial channels about one twelve-hundredth of an inch in cross-section is the size most generally used. The determination of the size of these channels is very easily made in the following manner: For example, we find that twenty sand grains laid in a line cover a space of one inch. This would give for a square inch four hundred grains with a corresponding number of interstitial spaces. Taking the proportion of voids or interstitial spaces in a given quantity of sand, which will be found to be approximately $33\frac{1}{3}$ per cent., we find that in each cubic inch of sand there are twelve hundred channels having a combined area of one-third of a cubic inch, which is equivalent to one twelve-hundredth of an inch for each channel. This

computation is, of course, subject to slight fluctuations, but as above stated the sand is so screened that there is very little variation in the size of the sand grains, and consequently the channels, although quite devious, must maintain a fairly uniform cross-section.

We have already seen that the finer particles of matter that must be retained by the filter range in diameter from one twelve-thousandth of an inch to one one-hundred-thousandth of an inch and we must retain these particles in a medium that has channels one twelve-hundredth of an inch in diameter. In other words, we have a screen with openings ranging from ten to eighty times that of the particles which must be retained. At first sight this appears to be an impossibility but an inspection of the filtered water shows that 99 per cent. or more of these fine particles have been removed. True, the addition of a coagulant has gathered together a great many of these particles into flocculent masses, but these masses have little cohesion and are broken up by the slightest agitation. Besides, a large number of the fine particles are not entrapped in the coagulated matter. Moreover, there are types of filters which run for long periods of time without showing the faintest visible trace of a surface film or blanket so that a hypothetical medium with fine interstices on the surface of the filter can hardly be held accountable for the high efficiency.

A thorough consideration of this rather paradoxical process of filtration brings forth the rather startling conclusion that the so-called mechanical filter is not in the strictest sense of the word a filter at all. We have been accustomed to regard the filter paper of the laboratory as the true type of filter and this to a great extent is true in that the pores in the paper are so fine that they are small enough to prevent large particles passing through.

To a large degree the slow sand filter acts in the same way as the filter paper because the layer of impurities at the surface, being formed of the impurities themselves, has smaller interstices which arrest all that come after.

Some other process must be possessed by the mechanical filter. Although difficult to demonstrate conclusively just what does take place within the depths of the sand bed the following is a plausible theory of the true process. The water delivered to the sand bed contains some more or less finely divided hydrate of alumina and other coagulated substances of a viscid or sticky nature. These particles of matter freely enter the large interstitial channels of the filter bed. In passing through these devious channels they sooner or later come into contact with a sand grain, to which they attach themselves. This may occur very near the surface or not until the matter has been carried several inches into the bed. As the sand is two or more feet deep the probability of any particle passing through such a depth without coming in contact with a sand grain is extremely low. After a few minutes' operation enough adhesive matter has attached itself to the sand grains to give the filter a high efficiency, that is to say, the sand grains have become coated with the adhesive substances derived

from the water so that any particles of matter which are not of a sticky nature would in turn become attached to this substance. This process of adhesion, or entanglement, or whatever we choose to call it, progresses for a period of time, say for some hours, and the channels keep getting smaller and smaller by reason of the quantities of material attached to the sand grains. This reduction in area of the channels first takes place near the surface of the filter. There is no indication on the surface of the sand of any impurities being retained, but if some of it is removed and placed in clear water it will be found that large quantities of matter can be washed from it. If a sample of sand is taken a foot or more below the surface it is found, during the early stages of the run, that there is very little foreign matter in it. In time, however, as the velocity through the upper layer of sand increases, due to the restriction of the area of the channel, particles of the retained matter are torn away from their anchorage and carried deeper into the bed, where, by reason of the greater area, the flow is reduced in velocity so that these particles can again reattach themselves. This process goes on until the voids in the top 12 inches of the sand bed are almost entirely filled with the impurities. At this period the resistance through the filter bed is so great that the velocity of flow cannot be maintained and in a very short time a surface film appears upon the filter, and the appearance of this film with some makes of filters is an indication that the filter bed must be washed, as the filter becomes impervious to water soon after its appearance. Samples of the sand taken from filters at different depths at different periods of operation seem to indicate the correctness of this theory.

The above conclusions have been arrived at after a number of experiments. In the first place, the writer has found that a very shallow filter, six inches in depth, made of the peculiar kind of sand used in mechanical filters, possesses a very low efficiency indeed. In fact it is hardly able to clarify the water. Again, in filtering other substances beside water, fresh cider for instance, that the filter sand has hardly any effect, although a filter paper would make the cider perfectly clear. Other fluids also show poor results.

Puech and Chabal have constructed a number of filters which in certain ways parallel this action of the mechanical filter. They differ in application, however, from the fact that they use a very much coarser medium with much greater interstices, and they filter the water repeatedly through several filters before the requisite degree of purification has been reached. The underlying principals, however, do not differ materially from those possessed by the mechanical filter, but there is a very decided difference in one point which is that the Puech filter has no method of cleansing and consequently the filter medium accumulates great quantities of foreign matter which is not of a sufficiently tenacious form to hold more than a portion of the finely divided matter in the water.

The mechanical filter consists of a suitable tank or container in which is placed the filter bed proper, which, as above described, consists of very carefully

screened sand. Rounded sand is preferable to sharp fresh quartz by reason of the fact that the active movement of the sand grains during the washing process tends to wear the corners off the sharp sand and decrease t in effective size. Underneath the sand bed is placed the strainer system, which is a series of strainers connected to suitable piping, whose office is to conduct the filtered water away from the sand bed and to distribute the wash water uniformly underneath it when the filters are being cleansed. Usually the strainers have orifices or ports in them smaller in size than the sand, but there are certain exceptions to this rule wherein large ports are used and the sand layer is carried upon successive layers of graded gravel. This latter plan is effective for a time but eventually the gravel layers become distributed and let more or less sand pass through, which, of course, enters the strainer piping and is very likely to obstruct it so that only a portion of the filter will wash. Also, sand in the filtered water is frequently very annoying in many industrial applications.

The filter must also be equipped with the necessary piping for reversing the flow of water for washing, filtering to waste and filtering. In the washing process the upward flow of water produces a rapid agitation of the sand grains which may be further increased by means of a revolving rake or by forcing air up through the sand. Occasionally a wash pump as well as a positive blower is required to assist in the above operation. Some filters must be washed with filtered water only while others possess greater latitude and can be washed with either raw or filtered water at will, there being a great advantage in favor of the filter which can use both, as it frequently happens that washing becomes necessary at a time when the supply of filtered water is greatly depleted, and it then becomes necessary to close down the entire plant while enough water wash is being accumulated.

If the filter plant is properly designed and the washing process is thorough, there should be no deterioration whatever of the filter bed, no deterioration of the quality of the effluent as the filter grows older, and no permanent accumulations of foreign matter within the filter bed.

It is inevitable that the streams in thickly populated districts should become the natural channels for industrial wastes. So long as we have industries so long must there be wastes which can be gotten rid of in no other practical way.

There are limitations to the burdens which can be placed upon manufacturers. Laws may be made which will stop the emptying of all wastes into streams, but these same laws will absolutely stop manufacturing, and in view of the fact that with certain very rare exceptions the most polluted streams can be used and reused for manufacturing purposes, the logical solution of the entire matter lays more within the remedial field than the prohibitive one.

THE NEW RESEARCH LABORATORY BUILDING OF THE AMERICAN ROLLING MILL CO., MIDDLETOWN, OHIO.

Received May 1, 1911.

The new laboratory building of The American Rolling Mill Co. marks a forward step in the development of industrial research.

The prime object of The American Rolling Mill Co. is to manufacture the purest ferrite iron that it is possible to produce on the large scale of operation permitted by open-hearth furnace practice. In addition to this, it is the intention to make this commercially pure iron the base of such useful iron alloys as may be demanded by future metallurgical development and discovery. The original attempt to manufacture an iron which should be practically free from carbon, manga-

office is adjacent to the main laboratory in front, and is convenient for overseeing the work.

In the basement is located the Storage Battery Room and Shop, which also serves as a terminal room for outside power.

The electric wiring system for the building was laid out to be as simple and flexible as possible. All wires are laid in conduits, and under benches a metal trough is used, which will take care of any temporary cables, which may be necessary for special work, thus keeping the main floor free from obstructions.

Practically all power and distributing wires, terminate in receptacles both on the main switchboard distributing panel and on benches and pedestals, thus making possible many combinations with plugs and cord connection at the main switchboard.

Two 125-volt sets of storage cells are controlled from one panel of the main switchboard, arrangement can be made for series and parallel working, and taps are brought out to receptacles in such a way that almost any voltage within the limit of the set may be obtained.

Another panel on the main switchboard controls the motor generator set, which is of special design for magnetic testing requirements. The motor is of interpole type, 7.5 H.P. capacity, having a speed ratio of 4 to 1. The generator gives a sinusoidal wave form, is 2.5 K.V.A. capacity, and is operated from seventeen and one-half to seventy cycles.

The Electrical Division of the Research Department is equipped throughout for complete tests on steel for magnetic and electrical properties. Modern apparatus is used but old types are retained and can be used at any time.

Permeability of sheets and solid bars can be determined by various methods. Watt loss and ageing tests are made on sheet steel; conductivity and coefficient tests can be made on bars of sheets.

Particular attention is given to the question of standards of precision. The Standards Room, Fig. 2, is

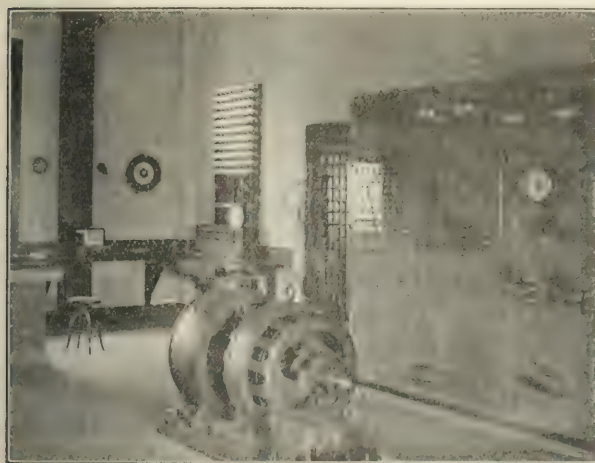


Fig. 1.—Motor generator and switchboard, Research Dept

nese and the other ordinary impurities found in steel, and still produce a metal unburned and degasified, presented a number of unknown difficulties and obstacles which only systematic investigation could be relied upon to solve. This situation led The American Rolling Mill Co. to organize a Research Department and build and equip a laboratory building in which investigation work could be carried on exclusively, without being burdened with the necessary daily routine of analysis and test. As a result of this determination, the company is now equipped at Middletown, Ohio, with one of the finest exclusively iron research laboratory buildings in the country, if not in the world.

The Electrical Division, Research Department.—Four rooms on the first floor and two in the basement are used by the Electrical Division of the Research Department.

The large main laboratory, taking up the entire width of the building, gives ample space for the main switchboard, motor generator set, and pedestals and benches for general testing. This room is shown in the illustration, Fig. 1. The Standards Room and routine test room, which are adjacent to the main laboratory in the rear, are equipped with benches, pedestals and test or auxiliary switchboards suitable for special work.

The Computation Room which also serves as an



Fig. 2 Standards room, Research Dept

equipped for this work only, and here are kept several instruments which are used for standardizing the instruments which are used continually in the laboratory.

Standard samples for various apparatus are kept on file in this room, which are used from time to time in checking up.

Metallurgical Division.—The Metallurgical Division of the Research Laboratory occupies the entire second floor of the building and consists of eight rooms as follows: office, distilling room, dark room, private research laboratory, main chemical laboratory, supply-room, balance room, and microscopical laboratory.

All rooms are heated with low pressure steam and are regulated by the Johnson system of thermostatic regulation to 72° F.

Electric terminals are so arranged in the various laboratories and rooms that any current from one volt up to 220 volts can be obtained at all times.

The chemical laboratories shown in Fig. 3 contain

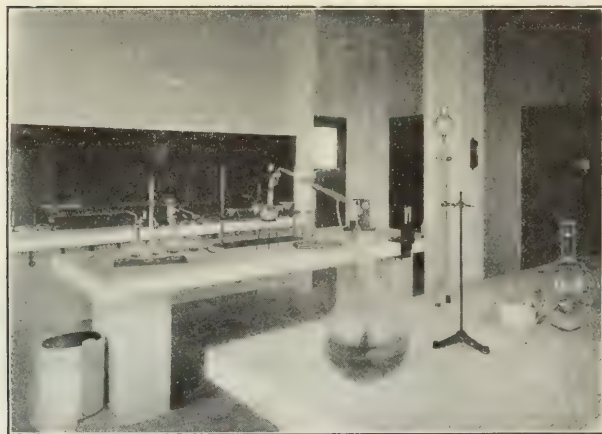


Fig. 3.—Chemical laboratory, Research Dept.

three vitreous enameled sinks connecting with terra cotta pipe to sewer. All sinks are fitted with three faucets, supplying hot and cold city water, and distilled water. The distilled water is furnished by a still in the building, heated by live steam, and has a capacity of ten gallons per hour, the still being located at an elevation of about ten feet above the floor, so as to give a sufficient head. It is connected by block-tin pipe to basement, and to all washstands of the building and tap in the storage battery room.

All gas, air and vacuum pipes in the chemical laboratories are embedded in concrete, the valves being placed beneath the table tops. Lead pipes are run from the laboratories to the basement where connections are made with gasometers from which various gases, such as oxygen, nitrogen and hydrogen can be obtained.

The shelves in the chemical laboratories beneath tables are suspended from the concrete table tops by iron bars.

The supply room shown in Fig. 4 adjoins the balance room on one side, and the main laboratory, being connected by double swinging doors. All shelves in the supply room, balance room and microscopical laboratory are of white carara glass. Supplies are un-

loaded in the supply room from a dumb waiter connecting with the basement storage room.

The balance room is located for a northern exposure, in order that the sun's rays would not interfere with



Fig. 4.—Storeroom filled with white glass shelves, Research Dept.

the eyes nor strike the balances so as to cause unequal expansion of the beams. In this room are located two Sartorius balances, one Torsion balance, and Harvard scale.

The dark room is fitted with double vestibule doors so as to exclude light, the bench tops are made of slate and contain the necessary equipment for photographic work. The window lights are double, consisting of the regular sash sliding vertically and glazed with amber colored glass. The other sashes are hinged and open into the room and are glazed with ruby glass. With this arrangement several combinations of light can be secured, viz., daylight, amber, ruby, or a combination of ruby and amber together.

One room is devoted to the Metallurgical Research Laboratory (Fig. 5), the floors, ceiling and table tops



Fig. 5.—Metallurgical laboratory.

in this room being faced with white tile. A hood 17 feet long occupies one side of the room and is lined with slate walls and tile table tops. This hood is partitioned off, the other half being located in the main chemical laboratory. A special feature of this hood is that it has a reinforced concrete outlet for the fumes and has openings on two sides and is also open at the top. The side openings allow the wind to enter, strike a baffle wall where it is deflected upward and creates a very good draught. The outlet is 4 × 8 feet and looks like a burial vault except for the openings. The hood is well lighted with windows glazed with florentine glass.

The main chemical laboratory is lined with white tile throughout, glazed tile for the walls and ceiling, and vitreous tile for floors and table tops. The vitreous and glazed tile were tested before selection.

Two tables, five feet by ten feet, of reinforced concrete faced with tile and supported by brick pedestals, are located in this laboratory, and furnish ample working space for many men. These are in addition to the bench which runs the length of the room on two sides.

The microscopical laboratory contains a reinforced concrete table in the middle of the room, covered with a single slab of white glass weighing 850 pounds. The working benches are also of reinforced concrete construction, covered with white glass.

One room in the basement is used for corrosion tests and is furnished with shelves for crocks, holding various solutions, and at this time several thousand samples are being tested under different conditions.

One accelerated test consists of suspending samples of various materials on half-inch glass rods which pass through bars at the end of iron spokes, which are screwed into a hub. These hubs are all on one shaft, which is run by a small stream of water flowing into buckets on a wheel similar in construction to a water wheel, which when filled with water automatically turn the wheel, Fig. 6.

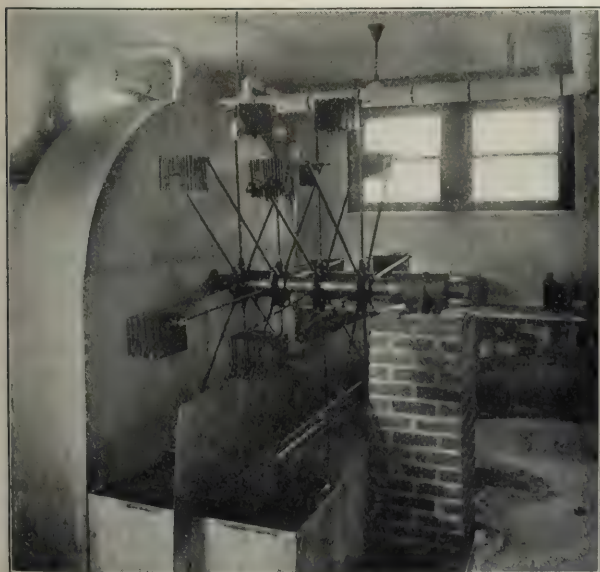


Fig. 6.—Wheel corrosion testing machine, Research Dept., known as the "Ferrous Wheel."

Three different tests are run on the wheel at the same time: one wheel dips the samples in well water, another in distilled water, and one in sea water. The wheel in turning exposes the samples immersed in the sea and well water to the air, where they are dried, while the distilled water samples are dried by burning natural gas which incidentally contributes carbon dioxide from the gas burned.

The apparatus throughout the laboratory is very complete and is of the best that the market affords.

An electric furnace of the electrode type is used in the Metallurgical Department, which is also equipped with an electric hot plate, silica tube furnaces, etc.

In the microscopical laboratory (Fig. 7) is a com-



Fig. 7.—Metallographic laboratory, Research Dept.

plete equipment for the microscopical examination of metals, and in this room is a spectrometer of the latest model for studying the gaseous impurities of iron and steel.

Hardness tests are made by the Shore scleroscope.

In the physical test division which is located in the basement of the Research Laboratory, the most modern equipment for the physical testing of iron and steel is installed. This includes a Riehle 100,000-pound tensile testing machine, the Landgraf-Turner alternating impact testing machine, a complete equipment for preparing samples, etc.

AN ELECTRIC FURNACE FOR ZINC SMELTING.¹

By FRANCIS A. J. FITZGERALD, Consulting Chemical Engineer, Niagara Falls, N. Y.

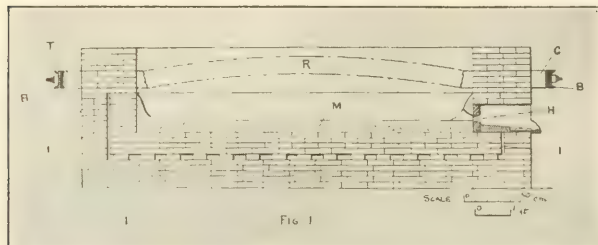
There is no branch of metallurgy which is apparently more suited to electric furnace treatment than that of zinc smelting. Moreover, the electric furnace possesses certain characteristics which make it specially applicable to the conditions of zinc smelting. It has long been known that when zinc sulphide and metallic iron are strongly heated the following reaction takes place,



but the reaction does not seem to be complete unless

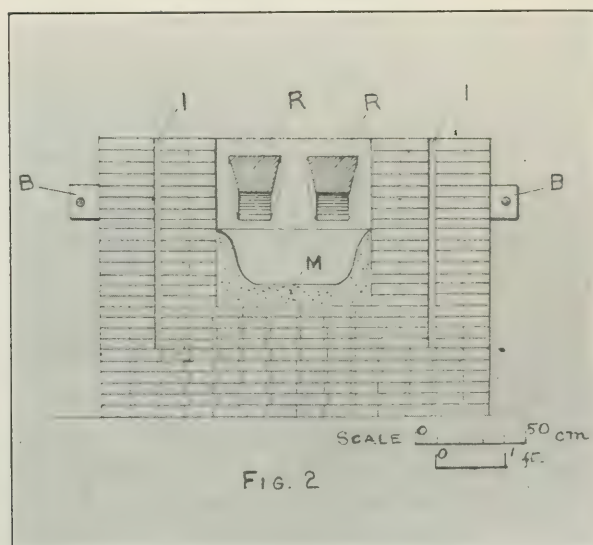
¹ Abstracted from a paper presented before the Congress of Technology at the Massachusetts Institute, Boston.

there is a relatively large excess of iron, or unless the temperature of the reaction is very high. Imbert, however, discovered¹ that by using suitable "dissolvents" this objection to the process is overcome. Imbert, for example, found that ferric oxide and iron sulphide mixed together in the proportion of one part and three parts respectively formed a very fluid bath at a temperature between 1000° and 1100° C., and that



this bath would "dissolve" six parts of blende. When the blende is "dissolved" in a bath in this way the reaction with iron mentioned above takes place with the greatest ease, is complete, works at a comparatively low temperature and as a residue produces two distinct substances—a slag consisting of the gangue from the ore and a ferrous matte which may be used for the regeneration of iron, etc.

(A great many experiments were made with this process and the results were highly satisfactory, except that it was very difficult to construct a suitable furnace for the purpose.) Obviously working the process in the ordinary zinc retort furnace would not be satisfactory, for the process should be carried out with a much larger unit than a zinc retort. When it comes to applying fuel heat to such a process numerous diffi-

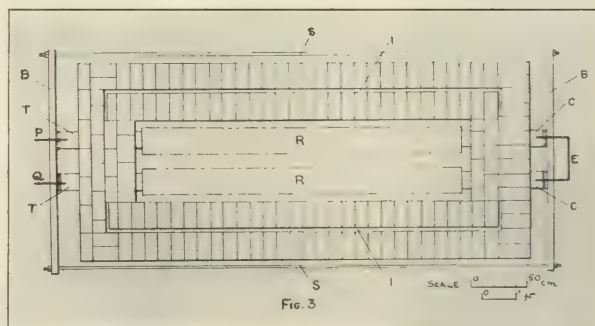


culties arise which are sufficiently plain without mentioning them in detail. This naturally led to the idea of using an electric furnace, and many experiments with various kinds were made. Finally Mr. John Thomson and the author designed a furnace which was used on a large scale in the working of the Imbert

Process. One of these furnaces of 150 kilowatt capacity was constructed and worked under the author's supervision in Hohenlohehutte, Upper Silesia, with highly satisfactory results.

In order to design a satisfactory furnace it was necessary to keep certain points in view: The furnace must be gas-tight; the temperature must admit of careful regulation; the construction must be rugged so as to stand severe usage; the heat losses must be reduced to a minimum since electrically generated heat is always expensive.

In Figs. 1, 2 and 3 are shown respectively a longitudinal section, transverse section and plan of the furnace with the cover removed. The walls of the furnace are double with air-spaces I which are designed to prevent the loss of heat by conduction through the walls. The furnace is provided with carbons, T, T, C and C, the two former serving as terminals which are connected to the source of current by means of cable indicated by P and Q, while the two latter are simply connector



terminals which form the other terminals of the two sections of the resister R, R, and are connected by E. Bearing on the terminals T, T and the connector terminals C, C are channels B, B which are connected with each other by the tension rods S, S. The channels are, of course, insulated from the terminals. The furnace is lined with a suitable refractory M and is provided with a tap-hole at H. The resister of the furnace is built up of a series of corrugated plates, which are illustrated in Fig. 4, the figure on the right showing an end view of the plate, while the one on the left shows the shape in which the plates are cut as viewed from the front. In Fig. 5 is shown a view of the plates set up so as to form a resister. Considering one of the plates it is to be noted that the thickness is not the same from top to bottom, but increases from the bottom up so that when put in place they form an arch of very long radius as shown in Fig. 5. Because of the interlocking of the plates this arch form is not necessary, but seems to be desirable in the preliminary assemblage and is also utilized to produce a somewhat greater current density along the lower surface of the resister. The cover of the furnace, which is not shown in the illustration, carries feeding tubes by means of which the ore mixture may be fed into the bath below the resister.

The peculiar construction of the resister plates has two purposes: to give a sufficiently high resistance to the resister and at the same time to form an interlocking device so that even if no arch form is given to the

¹ U. S. Patent 875,589, Dec. 31, 1907.

resister yet it will not fall down. A furnace was built with plates having these dimensions:

Length at top	405 mm	16 inches
Length at bottom	255 mm	10 inches
Width	165 mm	6.5 inches

The two sections of the resister contained 71 plates each. This when cold had a resistance of 0.200 ohm and when running at the full capacity of 150 kilowatts, and with a temperature in the furnace of 1400° C., the resistance was 0.0375 ohm. This resistance is due almost altogether to the contact resistance between the plates, for by calculating the resistance of the carbon itself we find that it would not amount to more than 0.00064 ohm.

In order to regulate the rate of generation of energy in the resister there must be some means of varying the voltage at the terminals of the furnace. At Hohenlohehutte, as well as in the FitzGerald and Bennie Laboratories where these furnaces have been worked, this is done by means of a transformer with several taps brought out from the primary coils which allow the voltage on the secondary circuit to be varied from 50 to 100 volts in 2.5-volt steps, and from 100 to 200 volts in 5-volt steps.

It will be seen that the weakest part in this furnace is the carbon resister, due to the fact that if working in an oxidizing atmosphere the resister will be destroyed. In the particular work for which it was designed, however, there would be no danger of this because the furnace is filled with vapor of metallic zinc. During the process of heating the furnace, or at any time when zinc vapors were not generated, there would be danger of burning through air leaking in; but this is easily overcome by keeping a reducing

The furnace is a highly efficient one. In one of the earlier models where the heat insulation was far from being satisfactory careful determination of all heat losses were made. When working at temperatures between 1250° and 1260° C. the total heat losses were 33 kilowatts, and when working at temperatures between 1400° and 1450° C. the heat losses were 42 kilowatts. Consequently when the furnace is working at full capacity, 150 kilowatts, the thermal efficiency at 1250° is 78 per cent. and at 1425° C. is 72 per cent. No exact determinations of the efficiency of later models have been made, but it is known to be much higher than those given above.

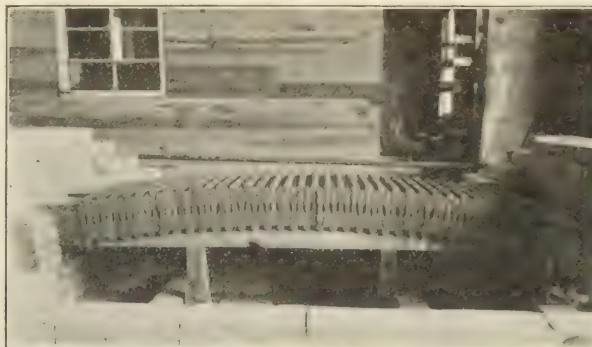


Fig. 5

The metallurgical end of the problem has not been completely worked out, but the satisfactory working of the furnace has been clearly demonstrated, and furnaces built on similar principles have been used experimentally with great success in the melting of aluminum, copper, brass, etc. This is thought to be of some interest, as a development in the use of electric furnaces using the heat generated by the passage of an electric current through a resister. There is a tendency in electric furnace work to employ the arc which is often a mistake because of the difficulty in regulating the temperature. Finally, the furnace described above from its construction lends itself readily to adaptations which permit of using the combined heat effects of fuel and electricity, and it is thought that a great future is in store for furnaces of that type.

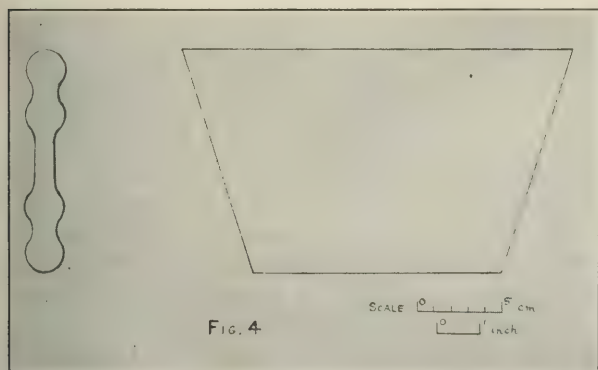


FIG. 4

atmosphere in the furnace slightly above external pressure. It has been found by actual experiment that a furnace of this type running continuously for two months showed no appreciable wear of the resister.

The regulation of temperature in this furnace is most satisfactory. In the Hohenlohehutte experiments thermo-couples or pyrometers were placed in several parts of the furnace to study the temperature conditions carefully. It was found that the most accurate regulation of the temperature in the furnace was possible, the workman in charge adjusting the rate of generation of energy in the resister so as to keep the needle of the pyrometer stationary.

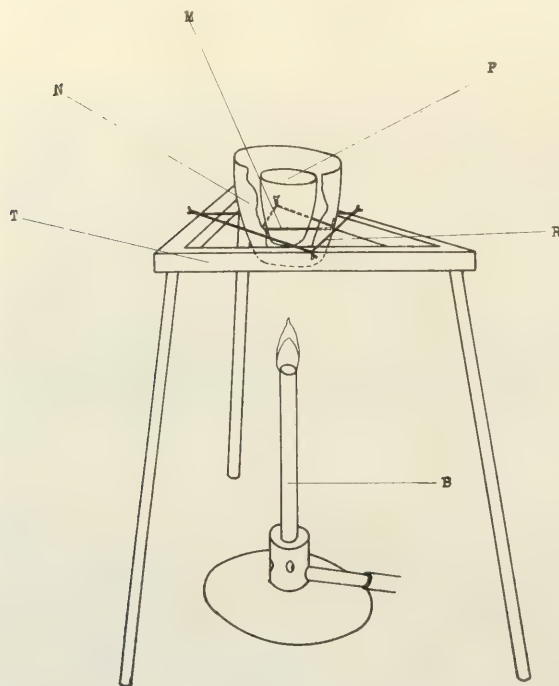
A RADIATOR FOR PLATINUM CRUCIBLES.

By W. M. THORNTON, JR.

Received March 16, 1911.

The accompanying drawing illustrates a very simple radiator for the evaporation of solutions to dryness in platinum crucibles. P is the platinum crucible, held in position by the Hoskins chemists' triangle M (a special nickel alloy). The ends of the Hoskins' triangle are cut off at a point about midway their length and bent upwards. The Hoskins triangle is supported by the walls of the nickel crucible N at a height that will hold the platinum crucible with its bottom and sides about equidistant from the bottom and sides of the nickel crucible. The outer crucible is supported by a triangle of nickel wire, R, which in turn rests on a tripod, T, of iron (coated with aluminum

paint). By placing a small flame under the outer crucible the inner crucible is uniformly heated by hot air, and its contents can be rapidly brought to dryness without danger of spattering. After the cessation of fumes the lid can be placed on the nickel crucible and the platinum crucible baked at an even and moderately high temperature if desired. The apparatus in use by the author is constructed of a "rein nickel" crucible of 100 cc. capacity and a $1\frac{1}{2}$ -inch Hoskins triangle. These dimensions serve very well for platinum crucibles



of 20 or 25 cc. capacity. The following advantages are claimed for the apparatus:

1. It can readily be constructed of materials obtainable by any chemist at small cost.
2. Nickel serves as an excellent material for a radiator because of its high conducting and radiating power. It is also very resistant to burning and rusting; and, hence, is very durable. The Hoskins triangle is made of a very refractory alloy in which platinum vessels can be held and heated with impunity.
3. Since the shape of the rein nickel crucible is approximately the same as that of the ordinary platinum crucible, all parts of the latter can be supported equidistant from the corresponding parts of the former thus securing uniform heating.

The author has found the above form of radiator especially useful in the analysis of some highly titaniferous rocks from Nelson Co., Virginia, in the laboratory of the Virginia Geological Survey. In separating the silica at 100° C. the titanium always hydrolyzes in large measure and precipitates on the separated silica. When the silica is subsequently determined by loss on evaporation with hydrofluoric and sulphuric acids, there is a considerable amount of solid titanium sulphate remaining. In conducting these evaporations on the hot plate, superheated steam and other vapors accumulated below a solid crust and much trouble was experienced on account of spattering. When the radiator was used, however, and with proper adjustment of the flame, spattering became a very rare occurrence.

The above description is given with the hope that it may prove of help to other chemists who may find it to their advantage to resort to a like expedient.

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ADDRESSES.

METALLOGRAPHY AND ITS INDUSTRIAL IMPORTANCE.¹

By ALBERT SAUVEUR, Professor of Metallurgy in Harvard University.

Received April 17, 1911.

Twenty years ago the science of metallography was practically unknown and it is only within the last fifteen years that it has been seriously considered by metal manufacturers and consumers as a valuable method of testing and investigation. That so much has been accomplished in so short a time is highly gratifying to the many workers, practical or scientific, who have contributed by their efforts to the progress of metallography.

To realize the practical importance of metallography, it should be borne in mind that the physical properties of metals and alloys, that is, those properties to which these substances owe their exceptional industrial importance, are much more closely related to their proximate composition than to their ultimate composition, and that microscopical examination reveals, in part at least, the proximate composition of metals and alloys, whereas chemical analysis seldom does more than reveal their ultimate composition. It will bear repeating that from the knowledge of the proximate composition of a certain industrial metal

or alloy we are able to infer its properties and, therefore, predict its adaptability, with a much greater degree of accuracy than if we knew only its ultimate composition. The analytical chemist may tell us for instance that a steel which he has analyzed contains 0.50 per cent. of carbon, without our being able to form any idea as to its properties, for such steel may have a tenacity of some 75,000 pounds per square inch or of some 200,000 pounds, a ductility represented by an elongation of some 25 per cent. or practically no ductility at all; it may be so hard that it cannot be filed or so soft as to be easily machined, etc. The metal microscopist on the contrary on examining the same steel will report its structural, *i. e.*, its proximate, composition, informing us that it contains approximately 50 per cent. of ferrite and 50 per cent. of pearlite, and we know at once that the steel is fairly soft, ductile and tenacious, or he may report the presence of 100 per cent. of martensite and we know that the steel is extremely hard, very tenacious and deprived of ductility. Which of the two reports is of more immediate practical value, the chemist's or the metallographist's? Surely that of the metallographist. Nor is it only in the domain of metals that we find such close relationship between properties and proximate composition, for, on the contrary, it is quite true of all substances. How many

¹ Abstracted from a paper presented at the Congress of Technology, April 11, 1911, Boston, Mass.

organic bodies, for instance, have practically the same ultimate composition and still are totally unlike in properties because of their different proximate composition, *i. e.*, different grouping and association of the ultimate constituents! If we were better acquainted with the proximate composition of substances many explained facts would become clear to us. Unfortunately the chemist too often is able to give us positive information in regard to the proportion of the ultimate constituents only, his reference to proximate analysis being of the nature of speculation. Ultimate analysis has reached a high degree of perfection in regard to accuracy as well as to speed of methods, and analytical chemists have built up a marvelous structure calling for the greatest admiration. Their searching methods never fail to lay bare the ultimate composition of substances. But how much darkness still surrounds the proximate composition of bodies and how great the reward awaiting the lifting of the veil! The forceful and prophetic writing in 1890 of Professor Henry M. Howe naturally comes to mind. Speaking of the properties and constitution of steel, Professor Howe wrote:

"If these views be correct, then, no matter how accurate and extended our knowledge of ultimate composition, and how vast the statistics on which our inferences are based, if we attempt to predict mechanical properties from them accurately we become metallurgical Wigginses. . . .

" . . . ; ultimate analysis never will; proximate analysis may, but by methods which are not yet even guessed at, and in the face of fearful obstacles.

"How often do we look for the coming of the master mind which can decipher our undecipherable results and solve our insoluble equations, while if we will but rub our own dull eyes and glance from the petty details of our phenomena to their great outlines their meaning stands forth unmistakably; they tell us that we have followed false clues, and paths which lead but to terminal morasses. In vain do we flounder in the sloughs and quagmires at the foot of the rugged mountain of knowledge seeking a royal road to its summit. If we are to climb, it must be by the precipitous paths of proximate analysis, and the sooner we are armed and shod for the ascent, the sooner we devise weapons for this arduous task, the better.

"By what methods ultimate composition is to be determined is for the chemist rather than the metallurgist to discover. But, if we may take a leaf from lithology, if we can sufficiently comminute our metal ('ay, there's the rub!'), by observing differences in specific gravity (as in ore dressing), in rate of solubility under rigidly fixed conditions, in degree of attraction by the magnet, in cleavage, luster, and crystalline form under the microscope, in readiness of oxidation by mixture of gases in rigidly fixed proportions and at fixed temperatures, we may learn much.

"Will the game be worth the candle? Given the proximate composition, will not the mechanical properties of the metal be so greatly influenced by slight and undeterminable changes in the crystalline form, size, and arrangement of the component minerals, so

dependent on trifling variations in manufacture, as to be still only roughly deducible?"

The above was written before the days of metallography or at least when metallography had barely appeared in the metallurgical sky and when no one yet had fancied what would be the brilliant career of the newcomer. Metallography has done much to supply the need so vividly and timely depicted by Professor Howe, precisely because by lifting a corner of the veil hiding from our view the proximate composition of metals and alloys it has thrown a flood of light upon the real constitution of these important products. Has the game been worth the candle? Will any one hesitate to answer in the affirmative Professor Howe's question?

Professor Howe with his usual acumen was conscious of the fact that proximate analysis, while likely to reveal a great deal more of the constitution of metals than ultimate analysis ever could, might still leave us in such ignorance of their physical structure as to throw but little additional light upon the subject. His fear was certainly well founded and surely if the proximate composition had been obtained by chemical analysis it would indeed have told us little of the structure or anatomy of the metals. In the domain of proximate composition chemistry can not do more for the metallurgist than it does for the physician. Chemistry does give invaluable information without which both the physician and the metallurgist would be in utter darkness, but it throws little or no light upon the anatomy of living or inanimate matter. Its very methods which call for the destruction of the physical structure of matter show how incapable it is to render assistance in this, our great need. The parallel drawn here between metals and living matter is not fantastic. It has been aptly made by Osmond who said rightly that modern science was treating the industrial metal like a living organism and that we were led to study its anatomy, *i. e.*, its physical and chemical constitution; its biology, *i. e.*, the influences exerted upon its constitution by the various treatments, thermal and mechanical, to which the metal is lawfully subjected; and its pathology, *i. e.*, the action of impurities and defective treatments upon its normal constitution.

Fortunately metallography does more than reveal the proximate composition of metals. It is a true dissecting method which lays bare their anatomy, that is, the physical grouping of the proximate constituents, their distribution, relative dimensions, etc., all of which necessarily affect the properties, for two pieces of steel for instance might have exactly the same proximate composition, that is, might contain, let us say, the same proportion of pearlite and ferrite and still differ quite a little as to strength, ductility, etc., and that because of a different structural arrangement of the two proximate constituents; in other words because of unlike anatomy.

It is not to be supposed that the path trodden during the last score of years was at all times smooth and free from obstacles. Indeed the truth of the proverb that there is no royal road to knowledge was constantly and forcibly impressed on the mind of those

engaged in the arduous task of lifting metallography to a higher level. Its short history resembles the history of the development of all sciences. At the outset a mist so thick surrounds the goal that only the most courageous and better equipped attempt to pierce it and perchance they may be rewarded by a gleam of light. This gives courage to others, and the new recruits add strength to the besieging party. Then follows the well-known attacking methods of scientific tactics and strategy, and after many defeats and now and then a victorious battle the goal is in sight—but only in sight and never to be actually reached, for in our way stands the great universal mystery of nature: What is matter? What is life?

Nevertheless there is reward enough for the scientist in the feeling that he has approached the goal, that he has secured a better point of vantage from which to contemplate it. The game was worth the candle. And if scientific workers must necessarily fail in their efforts to arrive at the true definition of matter, whatever be the field of their labor, they at least learn a great deal concerning the *ways of matter*, and it is with the ways of matter that the material world is chiefly concerned. Hence the usefulness of scientific investigation, hence the usefulness of metallography.

Like any other science with any claim to commercial recognition, metallography has had first to withstand the attack and later to overcome the ill-will and reluctance of the so-called "practical man" with a decided contempt for anything scientific. He represents the industrial Philistine clumsily standing in the way of scientific application to industrial operations. Fortunately, while his interference may retard progress, it cannot prevent it. Had he had his own way neither the testing machine, nor the chemical laboratory, nor the metallographical laboratory, nor the pyrometer would ever have been introduced in iron and steel works.

In metallography, as in other fields of research, American workers, with very few exceptions, have been quite willing to let Europeans perform the arduous and generally unrewarded task of the pioneer, being content to wait, before entering the field, until practical results were fairly in sight. Such course, which is never to be commended, becomes intolerable when accompanied, as it so frequently is, by the coarser boasting attitude of the man believing himself smarter than his neighbor whom he regards in the light of the cat drawing the chestnut from the fire. America, barring brilliant exceptions like Richards at Harvard and Noyes at Tech, does not as yet do her share of the pioneer's work in investigations which do not give evident indications of quick commercial returns. The unselfish, nay self-sacrificing spirit of the true scientist is of far rarer occurrence in the United States than it is in Europe and especially in France. America has not yet produced a Pasteur nor a Berthelot, intellectual giants, profound scientific thinkers, whose conception of the duty of the scientist as a man is so lofty that they have despised the wealth within their easy reach to devote themselves unreservedly to the betterment of their country or rather of the world, for they

are morally so great that the entire world becomes their fatherland: Humanity claims them.

Speaking in 1904 of the practical value of metallography in iron- and steel-making, I wrote the following which it may not be out of place to reproduce here: "History, however, must repeat itself, and the evolution of the metallographist bids fair to be an exact duplicate of the evolution of the iron chemist; the same landmarks indicate his course: distrust, reluctant acceptance, unreasonable and foolish expectation from his work, disappointment because these expectations were not fulfilled, and finally the finding of his proper sphere and recognition of his worth. The metallographist has passed through the first three stages of this evolution, is emerging from the fourth and entering into the last. For so young a candidate to recognition in iron- and steel-making, this record is on the whole very creditable."

We may say to-day that he has definitely entered the last stage and that the adverse criticisms still heard from time to time, generally from the pen or mouth of ignorant persons, are like the desultory firing of a defeated and retreating enemy.

In the United States alone the microscope is in daily use for the examination of metals and alloys in more than two hundred laboratories of large industrial firms while metallography is taught in practically every scientific school or technical school.

THE HYGIENE OF THE WHITE LEAD INDUSTRY.

By ALICE HAMILTON, M.A., M.D., Illinois Commission on Occupational Diseases.

Received April 13, 1911.

The Illinois Commission on Occupational Diseases made a study last year of the poisonous trades of Illinois, among which the lead trades hold by far the most important place. In the course of this work it was my task to investigate personally the white lead factories, and I visited ten such places in and near Illinois, eight using the Old Dutch Process, one the rapid modification of this process known as the Carter Process, and one the Mild or Rowley Process. During the summer and autumn I had an opportunity to see some white lead works in England, Belgium and Germany, and to compare the hygienic conditions in the white lead industry in those countries with the conditions in our own.

Like any American I went to Europe prejudiced in favor of my own country. It is true I knew that there was an admirably planned system of government control of this dangerous trade in Europe but I had been led to believe that such control was absolutely necessary in the older countries, that hand-work, the employment of women, the wretched physique of the workmen made necessary a sort of protection which would be absurdly superfluous here. I was destined to find that the reverse is true, that not only is the foreign workman protected against the dangers of work in white lead, but the dangers are not nearly so great with European methods as with American. In the following pages I will try to give briefly the difference between the methods used here and in Europe.

As far as the construction of European white lead and color works is concerned compared with ours, I should say that their best was not as good as our best, nor their worst as bad as our worst. Nowhere did I see a white lead plant as admirably built as some American factories, with their concrete walls and floors. On the other hand, the most antiquated and economically managed factories there cannot be as bad as some of ours are, because the law insists upon certain essentials in structure. For instance, there is a factory in Chester which is 143 years old and looks it. The buildings are low and shabby, irregular and dark, but the stacks are built of brick, glazed on the outside, the floors are of stone or of sheet iron, the water supply throughout is adequate so that the floors may be repeatedly flushed, the lavatories, bathrooms and lunch-rooms are what they should be, all of these details being controlled by the Home Office. A manufacturer may let his plant run down in any other way, but he may not let it become a dangerous place to work in. In Germany the same thing is true, in Belgium it is only partially true. State control there does not seem so strict.

The standard of cleanliness is not as high as it is in our best factories, though of course it is never allowed to fall as low as it does in some of our worst.

One thing which state control brings about in Europe is the complete separation of dusty from non-dusty operations. You will never see there, as you sometimes see here, dry packing or mixing carried on in the same room with the filling and labeling of white paint kegs.

Machinery has reached a high point of development, a fact which came to me as a surprise for I had repeatedly been told that I should find hand-labor everywhere in Europe. There are some places where processes are still done by hand which can be done mechanically, but in the best factories hand-work has been superseded by machinery as much as it has with us. For instance at Debbaudet Bros., in Brussels, where the process is more nearly like ours than in any other place I saw, there is as little hand-work as possible and there are all sorts of most ingenious devices which I have never seen in any other place. In the red lead department of Cookson's, in Newcastle-on-Tyne, machinery is used to the same extent as it is here and in Leyendecker's, in Cologne, it is much more highly developed, human labor seems almost eliminated.

For those who are not familiar with the Old Dutch or Stack Process for making white lead it may be best to give a brief description of this process as carried on in the United States. Pig lead is melted and cast mechanically in the form of "buckles," thin plates with open spaces and cross-bars, in shape resembling old-fashioned shoe buckles. These are conveyed to the stack house, a more or less open building divided into compartments or stacks, with concrete or wooden partitions. Here the buckles are placed in earthenware pots which contain dilute acetic acid and laid in rows upon a bed of spent tan-bark and covered with boards. Another layer of bark is placed on these boards and then another layer of pots and so, on until

the stack is full. It is then left untouched for about 90 days when the acetic acid vapor together with the CO_2 from the fermenting tan-bark has converted the lead into the basic carbonate, white lead. Uncovering and emptying the pots of white lead is a dusty and very dangerous piece of work. These "corrosions" are then carried in trucks, by hand or by crane, to the "dump" which is a large opening, with usually a very inadequate exhaust system, into the separating apparatus. Once inside the separator the lead is not a source of danger for the machines are tightly enclosed, and only the repairing machinist need run any risk in this part of the process. The separating is effected by means of rollers and screens, and the final products are white lead powder which is discharged into water, and fragments, large and small, of "old lead" or uncorroded buckles which are covered with white lead and very dusty to handle. In some American factories it is customary to remelt these and they are usually shoveled into open trucks, wheeled to the casting-room where they may be dumped to lie on the floor till they are needed or put at once into the kettle. In other places the "old lead" is given a second corrosion in the stacks. All this handling of dry fragments is dangerous for the men.

After it has passed through water mills, bolting machines and settling tanks, the white lead is pumped into great drying pans which stand one over the other in a hot room. At the end of about five days the water has passed off and the powder is ready to be shoveled out and conveyed to the barrels or the oil mixers. This is the most dangerous spot in an American white lead factory, and although I have seen some effort made to diminish the dangers I have never seen a drying room which was even moderately safe. The other dangerous jobs are the barrel-packing, which is mechanical but always accompanied by dust, heading up barrels, filling chasers (oil and lead mixers) which in some factories are well covered and free from danger, and the work in the dust-collecting room which is always attended with risk. In a well-managed American white-lead factory there are always some dusty, dangerous processes; in a carelessly managed one there may be no spot in the factory where it is really safe to work. Dry sweeping is the rule in almost all the American factories I have seen.

In England and Europe the Old Dutch Process has developed differently in many details.

Nowhere are buckles cast, always long strips, sometimes solid, sometimes with three or four holes, sometimes with depressions like a long waffle. They are often eighteen inches long and an inch thick. At Locke-Lancasters each strip weighs four pounds. The pots are small and the strips are either piled in layers on top of them or they are bent on themselves and laid edgewise on the top. English factories do not set stacks with cores from former corrosions, they always send these to the melting pot, but in the Brussels factory the cores are used to make the top layer of each set of pots. This is, of course, a disadvantage from the hygienic point of view, although the danger is lessened by drenching them before they are handled.

The Old Dutch Process is used in Belgium and almost everywhere in England. At Cookson's, in Newcastle, I found both Stack and Chamber processes in use, and the management much more enthusiastic for the latter. In Germany it is all Chamber Process, which means that the strips of lead are hung in large chambers into which steam, acetic acid vapors and CO_2 are conveyed by pipes.

It was only in the filling of the stacks that I saw women employed anywhere and this was in an old factory in Chester, where they still have women carry baskets of tan-bark up ladders to the stacks. Their employment is prohibited in any part of the work where white lead is handled, and though many manufacturers told the Parliamentary Commission that they would be driven out of business if such a law were passed, they seem to have been agreeably disappointed.

In Germany and England stacks and chambers must be thoroughly watered before they are emptied, so that there will be no dust. From then to the final drying, all the process is wet. The big corroded strips are picked up and laid in wooden trays and then are carried on trucks to the separator. As a further precaution against dust each tray is rapidly plunged into water, "baptized" they call it, or sprayed with water, before being emptied into the separator. Separation is done by washing and does seem very simple, far simpler than our dry method. Sometimes it is done by hand, as in one of Locke-Lancaster's plants where 15 tons are separated in a day, in others it is done by mechanical crushing in water. But it consists simply in washing the white light powder from the heavy solid core which falls to the bottom, while the water and white lead pass on, first through metal sieves, then through two sets of granite stone mills, then through silk sieves to the settling tanks.

From the point of view of the hygienist this method is so much better than ours that one longs to see it adopted here. I cannot, of course, speak of it from any other point of view, although to an outsider like me it does seem economical and sensible. There are no small particles to be gotten rid of as from our corroded buckles, only large solid cores. And they do not aim at anything like complete corrosion. Locke-Lancaster's foreman stated that 36 per cent. to 50 per cent. corrosion was what they expected.

From here the process varies in different factories. In some of the less advanced English plants, the product of the last settling tank, now a thick soup, is ladled into shallow trays which are carried to the shelves of the drying rooms. In the best factories, such as Cookson's, Locke-Lancaster's, and Leyendecker's, it is pumped by means of compressed air into a vacuum receiver where it is forced through filter presses, and all but 16 per cent. of the water removed. This paste then is partly used for the making of pulp lead, in England, or sold as it is in Germany where pulp lead is never sold. The rest is put into shallow trays and these are laid on trucks which are wheeled into drying cells. A high temperature is maintained here, and after three days the white lead is dry. Then the trucks are wheeled out, the workman only opening one door at a time, and not stepping inside the cell.

The trays are then lifted one by one and emptied through a small opening which is variously made but always protected by a hood and an exhaust. The cleverest arrangement I saw was in Brussels where the tray was set on a shelf into which it fitted tightly. This was tipped over under a hood, and then tipped back again. Cookson's has a different drying process which they worked out independently, in their effort to get away from the dangers of the old-fashioned stoves. They shovel the paste into furnaces, and the furnace room is beautifully clean and well-ventilated. The furnace is emptied by means of a long-handled shovel which passes through a canvas bag. The top of the bag is fastened to the edge of a hood with an exhaust, which is right over the door of the furnace, and the bottom falls over the truck into which the dry powder is being shoveled. There is absolutely no escape of dust.

The dry white lead as I saw it was much harder, more porcelain-like than ours is, and the Europeans insist that you cannot get it bone-dry by our method.

You can see what an enormous contrast there is between their methods and ours as far as danger is concerned. In the best factories, handling of the dry product is accompanied by practically no dust; in the worst the dust is slight in amount, while I have never seen an American drying-room which was even moderately dust-free.

Barrel-packing is done as it is here, in most places, and again I should say that it is nowhere as careless or dirty a process as I have seen it here, and nowhere as clean as I saw it in one American factory. In Belgium I saw an interesting device. The barrel—stronger and better built than ours—is already headed up and the lid has a round hole some six inches in diameter. Into this is fastened one end of a strong rubber tube the other end of which is hanging from the bottom of the white lead hopper. As the powder falls into the barrel it is shaken down because each barrel stands on a platform which is made to jump up and down by means of compressed air. I saw a whole roomful of barrels in process of filling and not a particle of dust. These of course need no heading-up, another great advantage. Heading-up is considered dangerous work and all sorts of devices are being experimented with. In Germany, as in some of our factories, each barrel is lined with strong paper which is folded down over the top before the lid is put on. In an English factory they are trying a lid with expanding leaves, which fit into place without hammering. I may add that no European country will allow shipment of leaky barrels or barrels smeared with white lead dust. In England the manufacturers are in favor of the Home Office forbidding the sale of dry white lead. They consider the objections to pulp lead a mere matter of prejudice. In Belgium the state allows the sale of dry white lead only to certain accredited color houses.

All chasers are enclosed and provided with exhaust and "enclosed" does not mean that there are large windows in the sides which are habitually left open is often the case here.

The process in Belgium differs from those I have described, and is more like the American because separation is done dry, and the stacks are not sprayed

before stripping. However, the buckles or rather strips, are lifted by hand, not dumped, and are carried in trays to the separator. I have already described the clever arrangement for preventing dust at the separator opening. The dry cores drop out from the separator under a falling lid with a good exhaust. They are taken in covered trucks—no open trucks of dry corrosions are found anywhere—and are used to set stacks, being put on top of the layers of blue lead. Dust collection is not needed in English and German factories, but in Belgium it is necessary, and in one place I saw it done in a very novel way. There is a tightly-built little brick house in one of the rooms and the dust which enters it is driven by means of fans against some curtains of heavy felt which hang from the ceiling and are kept wet by means of a spray of steam. The moist white paste is scraped off these curtains, which never are allowed to get dry, so that the dust house is really not dusty at all. It seems to me the simplest and certainly the safest device I have ever seen.

As to the hygiene of the white lead industry, many of the processes I have been describing have been devised in the effort to do away with the dangers inherent in the work, and here Cookson's led the way. In fact, the Home Office rules of 1883 were modeled largely on the practice obtaining then in Cookson's plants. That seems to me a very proud record for a commercial house.

The study of the past 30 years has shown that lead enters the body through inhalation and swallowing, not through the skin to any important extent. The English lay more stress on inhalation than the Germans, claiming that lead is absorbed by the blood vessels of the lungs, while the Germans think that what is breathed into the mouth is swallowed.

Of course the methods of protection are founded upon these facts and resolve themselves into suppressing the dust and seeing to it that the workman is free from white lead when he eats his lunch and when he goes home and that he does not carry it into his mouth while at work by chewing tobacco.

The abolition of dust I have already described. The care of the workman's person consists in supplying washing and mending his working clothes, supplying head-covering and sometimes shoes. At Leyendecker's all the men wear wooden shoes while at work, which is a splendid protection against the damp, cold floors.

Everywhere the men are provided with proper washing facilities and, not only that, but they must, by law, be given sufficient time to wash up, and all those who are engaged in the dustier processes must bathe every day. There is a bathing record kept, and it is a case of no bath, no pay. A man must show his bath receipts, so to speak, before he receives his wages. In the less dusty processes the workman need bathe only once a week.

Washing arrangements there are not as luxurious as they are here. On the other hand they are very much more carefully planned. The Englishman does not waste his money on luxuries, so you will not find as beautiful sanitary equipment there as you may

find in this country, but the Home Office sees to it that he gives the employees what they need. The men have usually individual towels, numbered with each man's number to prevent stealing. There are long porcelain-lined sinks with no stoppers, so that a man must wash in clean running water. Usually big cans of soft hand soap are provided. There are sprays for the head attached over the sink, and long nail brushes are fastened to the wall just above the basins. The great difference between our arrangements and these does not lie in equipment, but in the fact that the foreign workman's personal cleanliness is compulsory, his employer is held responsible for it; the American workman (usually a Slav, Italian, Greek or negro) may wash or not, as he sees fit.

The lunch-rooms are not at all luxurious but there is always provision for heating food. Europeans insist that it is very important in white lead factories that the men should not go to work fasting, for nothing so favors lead-poisoning as that, and there is no better safeguard against it than the presence of food in the stomach. So we find always in England and on the Continent a half-hour given in the morning for breakfast. American employers if they inquired would find that their foreign-born workmen, and so many of them are foreign-born, need that pause for breakfast, for they are not accustomed to the hearty breakfast that fits the American workman to keep at work till noon. Another thing that struck me over there was the strict prohibition of tobacco-chewing. Wherever I have been in this country in white lead or red lead, or dry color establishments, or paint factories, I have asked the foreman whether he encouraged tobacco-chewing among his men, and I think there have hardly been more than one or two exceptions to an affirmative answer. Many a time the foreman says he teaches his men to use it. I find also that it is the opinion held by practical painters that the constant expectoration keeps the mouth free from lead dust. Tobacco-chewing is forbidden in Europe and in England because they say that the plug of tobacco is carried in a man's dusty clothes, his working clothes, and that it is taken out with lead-smeared fingers and passed into his mouth often through a lead-smeared mustache. The rules as to this are very strict. I was in one lead establishment with an inspector from the Home Office, and he wanted to test a certain exhaust and asked for a match. The foreman had none but one of the workmen had. The inspector told me later that as he was on a visit of courtesy he did not follow up the match episode. I asked him what he meant, and he said that any workman who had a match about him no doubt had some tobacco too, and that he always investigated such incidents.

Medical inspection is required by law over there. It is gratifying to know that many American white lead factories now have medical care for their men, but they have not yet taken the next logical step, which is that the medical inspector be told to weed out the men who are unduly susceptible to lead poison. A certain number of men cannot stand exposure to lead. Hirt, a great German authority, says that about 20 per cent. of all lead workers are over-susceptible and should

never attempt to do such work. The English and German physician examines all applicants for work and rejects the weakly and anemic. It is also the rule that a man once really leaded shall not return to a dangerous part of the work. Here, I find in a great many places that a man drops out because he is poisoned and goes home or to a hospital, and when he has recovered he is allowed to go back to exactly the same sort of work.

Of course in many ways it is much easier to manage men who are of the same nationality as their foreman and who speak the same language, as is the case in most foreign factories. On the other hand, I was told that the Italian help employed in one English factory were more docile than the Englishmen, who are sensitive about their individual rights and do not like to be controlled as far as personal habits go. It would certainly seem possible to make our men as amenable to discipline in the matter of cleanliness as in the matter of other factory rules.

It may be asked, What is the result of all this elaborate regulation in England and Europe? I have been told by American manufacturers that there is actually less lead-poisoning here than over there. Fortunately it is possible to answer that quite definitely. In Cookson's plant in Newcastle where 182 men are brought in contact with white lead, the most rigid weekly medical examination did not reveal one case in the year 1909 to 1910. In Locke-Lancaster's place there was not one case among 90 men for the five years between 1903 and 1908; there was one in 1909.

Let us look at our factories now. I can give partial statistics of six places which manufacture white lead, and when I say partial, I mean that in none of these factories is the whole truth about the men known. Three of them have the physicians examine all of the men employed in handling lead, but do not follow up those who quit work—the English and German laws require this to be done—a third factory has a physician see only those men who complain or whom the foreman suspects of illness, the other two have no medical inspection and the only way I have been able to find any cases has been through hospital records, and the men who go to hospitals are only the very severely poisoned, who have no families to care for them.

These are the statistics:

In Factory No. 1, medical examination showed one man in eight to be at the time suffering from plumbism.

In Factory No. 2, one man in nine.

In Factory No. 3, 28 per cent. of all employees have been leaded.

In Factory No. 4, where medical examination is only on complaint, 25 cases occurred among about 200 men, or one man in eight.

The two factories which have no medical inspection¹ are sending to a public hospital three cases and four cases respectively a month. This would mean 36 cases for one during the year and 48 for the other, but we know that not one-half of the leaded men go to the hospital and that the actual figure would be so much larger.

¹ One has recently engaged a physician to examine all the men regularly.

In the whole district of Newcastle-on-Tyne there were employed last year in the white lead works, 1320 persons and only five suffered from lead-poisoning, or one for every 264 employed. In Illinois last year there were from 425 to 450 men employed and we discovered sixty-three cases of lead-poisoning, or one for every seven men employed. This is a startling contrast and one that should make the American manufacturer stop and think.

POTASH FROM FELDSPAR.

By B. HERSTEIN, Technical Expert of the Tariff Board.

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The recent controversy between the German producers and the American importers of potash salt, a controversy which involved also the governments of both countries, has brought out forcibly the monopolistic privileges enjoyed by Germany through the sole possession of potash deposits and has emphasized the fact that most of the other nations, our own pre-eminently included, have to depend entirely upon that country for their supply of this absolutely indispensable plant food.

Irrespective of the economic aspect of the questions involved—and this is big enough even though we are accustomed to figure in big units—it must be admitted that the situation created by such a condition is far from satisfactory, and has naturally led numerous investigators to work on the subject.

It seems to have become an established fact that of the very few mineral deposits in which the United States, otherwise so bountifully provided, are deficient, potash in agriculturally available, *i. e.* soluble, form is one. However, potash in the form of insoluble silicate or aluminate makes up no inconsiderable part of the weight of feldspar and similar rock formation, and of these the supply in this country is practically limitless. As a plant food, however, the potash in this natural form is not assimilable and therefore of little value. The gist of all the many proposals so far made to secure from domestic sources the necessary potash salts required for agricultural purposes has consequently centered in the use of these rocks as raw material, differing only in the form proposed to render the potash available. The literature on the subject is fairly abundant and easily found in patent, technical or scientific publications.

As far as the chemistry of the problem is concerned the field seems to have been covered fairly well, and in submitting an additional proposition in this direction, the fact is not overlooked that taken separately the individual features of this proposition may present little novelty, emphasis being laid on their combination, which is absolutely essential, and appears not to have been suggested before. Those who have given the subject more than casual thought know also that the problem is more than chemical and more than commercial, and the plan is submitted here solely with the intention of broadening the legitimate scope of discussion by presenting possibly new and

important features towards a solution to a complicated problem.

The chemical reaction involved in the process as proposed needs no further elaboration, having been proved in practice; it is in fact being used in somewhat modified form as an analytical method for the determination of alkalis in silicates. It consists in heating the finely ground feldspar with calcium chlorid eventually under addition of some limestone, whereby the silicate is decomposed with the formation of alkali chlorides—readily removable—and calcium silicate or aluminate. The process differs, as can be seen, from the well-known Lawrence Smith method only by the fact that the calcium chloride is used here directly, while in the other the silicate is heated with a mixture of ammonium chlorid and calcium carbonate, which reagents form calcium chlorid as an intermediate product and thus bring about the decomposition of the silicate. Experiments have shown that the reaction can be carried through and decomposition of the feldspar accomplished with little more than the theoretical amount of calcium chlorid if the ingredients are intimately mixed and the temperature well regulated and maintained for a sufficiently long time. Increasing temperature requires a corresponding excess of calcium chloride.

Cushman, working along the same lines without adding limestone, seems to have made the same experience and rejects the process merely because it is too expensive, as indeed it would be if there were no other considerations, to mitigate and outweigh this otherwise justifiable injunction.

In the first place, the calcium chlorid required for the reaction is a waste by-product obtained in huge proportions in the manufacture of soda ash and salt. It is less than valueless and the owner, if assured of a continuous outlet, could well afford to let it go at a nominal price.

Secondly, the residue left after the potash has been removed, by aqueous extraction or otherwise, contains all the essential elements of a cement into which it could be transformed by ignition, supplementing the deficiency of calcium oxid with limestone, if required. No previous grinding would be necessary in this instance, since with the temperature kept reasonably low, the mass does not clinker and disintegrates easily in water. Moreover, both the silica and the alumina of the original feldspar have been rendered extremely reactive and should therefore readily form cement on the subsequent operation.

Another way to carry out the process would be to combine the two stages into one, *i. e.*, add limestone and an excess of calcium chlorid to the finely ground feldspar and heat the mass to clinkering, whereby the potassium chlorid would be driven out by the higher temperature and could be collected in a suitable way. The heat prevailing in a rotary cement kiln should prove amply sufficient to produce this result. The cement clinker would be formed simultaneously with the distillation of the alkali chlorid and would need only final grinding. In this form the process would not differ materially from

the ordinary way of making cement except in the presumed condensation of the alkali chlorid.

The plan as outlined, if feasible in any form, would accomplish:

1. The utilization of the valueless waste product, calcium chlorid, which at present is but a source of annoyance and expense.
2. The production of cement.
3. The production of potash salts for both industrial and agricultural purposes—a combination of three important features which should bring the proposition within the range of practicability.

The plan is embryonal, of course, as any plan of this character, based mostly on *a priori* consideration, must be. The problems involved are vast and touch materially the interests not only of great industries but presuppose also careful consideration and coöperation on the part of different sciences: chemistry, engineering, geology and—not the least—economics. The difficulties militating against the realization of any proposition to utilize the gigantic stores of potash compounds lying unavailable in the feldspar and similar rocks are great and should not be underestimated. A review of the more important objections may help to a better conception of the subject.

First, as to the supply of the principal raw material itself. Feldspar, it has been stated, is most abundant in many of the states and will undoubtedly be found in others. But, unfortunately, the deposits are compact only in isolated instances, more frequently, however, they are contaminated with quartz and the mineral requires picking before it can be put to its proper use. Also the percentage of K_2O varies within wide limits, some being as low as 5 per cent. and even under, others about 10 per cent., and some considerably above this figure. An average yield of 6 per cent., or 120 pounds of K_2O per ton, would probably be a safe limit to calculate upon; and this would be obtained in the form of potassium chlorid. This is not the most desirable and therefore not the highest paid form of potash for agricultural purposes, yet it is used very extensively. The above yield would correspond to 190 of KCl per ton of feldspar, the money value of which on this side of the Atlantic is at present, according to the price set by the German syndicate, \$4.50.

This sum is contingent upon one factor which requires consideration. The valuation of potash salts, at least for the export trade, is fixed, quite arbitrarily it seems, by the German commission entrusted with this task according to the law passed last Spring by the German Reichstag, which abolished all competition for trade between the individual mine owners. The monopoly is most complete and it is fair to assume that we are paying monopoly prices irrespective of the cost of production. The fact that individual operators contracted to furnish potash salts for some years to come to American importers at prices considerably lower than those fixed later by the commission, seems to support this interpretation, and the potash value of \$4.50 per ton of feldspar holds true

only as long as the Germans see fit to maintain their present prices.

As a potash proposition alone any attempt to utilize our feldspar as raw material offers therefore little attraction because a return of \$4.50 per ton would barely more than cover the cost of the raw materials themselves, *viz.*, feldspar, calcium chlorid, limestone and coal. But each ton of feldspar is assumed in the plan also to produce five and possibly six barrels of cement of an average value of \$4.80, which would bring the total returns up to \$9.30 per ton of feldspar. Is this sum sufficient to pay all the expenses and allow also some interest on the large investment that would be required? In answer to this it could be pointed as a parallel that cement is now selling at not much more than about \$4.50 per ton, and yet seems to pay at that price for the raw materials, cost of operation, etc., and only quite recently it has been stated by no less an authority than Dr. McKenna that the actual cost of materials and labor is about 12 cents per 100 pounds of cement. The \$4.50 obtained for the potash would, therefore, have to cover only the additional cost of the feldspar, the cost of some 200 to 250 pounds of calcium chlorid, a small additional charge in operation, and the interest on the additional investment required to provide for the collection of the potash salts. All evaporation, it is figured, is to be done by the waste heat of the kilns. Another item of extra expense would undoubtedly be found in the heavier freight charges because the raw materials would have to be brought together from different localities which is not the case in the cement industry.

An important factor to be considered is, to what extent such an undertaking would influence the cement industry, which already faces serious competition on the part of iron and steel manufacturers. Our present consumption of cement may be said to be about 65,000,000 barrels per year, but is rapidly increasing. The calculation as given above assumes for every ton of 80 per cent. KCl made, a production of 44 barrels of cement. Last year's imports of potassium chlorid alone amounted to over 160,000 tons, which, on the above basis, would be equivalent to 7,040,000 barrels of cement. Could such vast quantities be gradually added to a market which seems already overprovided, without creating an alarming disturbance? Can it be expected that within reasonable time things would adjust themselves to the new conditions, or could this new industry be established and maintained only by inflicting serious losses upon one already existing?

In the face of these difficulties it must be candidly admitted that from a purely commercial point of view, *i. e.*, as a question solely of profit and loss, the proposition as outlined above is not very alluring; nor for that matter any proposition so far advanced looking towards the utilization of the potash in the feldspar. The investment required and the risk assumed are unproportionately large compared with

the eventual stake. But the problem is not purely commercial, should not and cannot be considered so without ignoring the larger economic questions involved. The days of extensive agriculture—an anachronism under any condition in an age of chemistry such as ours—have passed in this country through natural limitations, and the years to come must see in the United States a rapid development of intensive agriculture if we don't want to become dependent upon other nations for some of our food supply and face all the serious consequences which such a condition implies. This means a more extensive use of fertilizers, more phosphates, more sulphuric acid, more nitrogenous compounds, and more potash salts. Our phosphate deposits are enormous. One-half of the sulphuric acid made in this country, or at present over 1,000,000 tons, goes into agriculture, and while the larger part is made from imported pyrites, there is more sulphur driven into the air in our western smelters than all our requirements call for, not counting the rich and readily accessible sulphur deposits in Louisiana. The fisheries and the slaughter-houses furnish vast quantities of nitrogenous matter which are being steadily increased by the gradual enlargement of the numbers of by-product coke ovens. With the rational development of water powers the fixation of atmospheric nitrogen on a large scale is only a matter of little time in this country. No fear need therefore be entertained on that score. For potash salts alone, every pound of it, we must depend on imports, paying at present yearly about \$8,000,000, a sum which is bound to go on increasing, even if the Germans should forego the temptation to raise prices, which always goes with monopolistic possession. To prevent this we would be absolutely helpless, unless through the adoption of some plan for utilizing the latent potash in the rocks we devise some means of checking such tendencies. By creating a new industry and developing our dormant resources more useful employment would be provided, which are other considerations of importance not to be neglected in any economic appreciation of the situation.

The problem as a whole, though fairly clear in its outlines, is yet far from being sufficiently concrete to promise any development from individual initiative alone. It is too broad and involves too many far-reaching questions of science, industry and national husbandry to admit of a solution on the part of any single person. It is a national question and should be treated as such. If any advance is to be made at all, it can come only from an authoritative body of men commissioned to investigate the whole field of the potash supply question in this country, a commission to include men of science with minds practical enough to distinguish between the economically feasible and visionary or impossible, and men of business capable of weighing a question from a viewpoint broader than merely that of profit and loss.

RESEARCH AS A FINANCIAL ASSET.¹

BY WILLIS R. WHITNEY, Director, Research Laboratory, General Electric Co., Schenectady, N. Y.

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It is only in our century that there could be much significance to such a title as "Research as a Financial Asset." This is an industrial century, and, whether we are proud of it or not, we are an industrial people. For some reasons it may be thought unfortunate that so large a proportion of man's energies should be devoted solely to the industries. In some eras we find that there was a predominance of art over industry; in others, literature was predominant; in still others, war and conquest. Once territorial discovery and acquisition predominated, and now, in our own times, the principles of community interest have so greatly developed that we are accustomed to seeing many people who, instead of directly producing their own necessities of life, are more generally repeatedly producing some one little article which contributes in the lives of others. This we recognize as a natural tendency to higher efficiency. Our intricate and delicately balanced system of work is becoming continually more complex, but is certainly still covered by the elemental laws of demand and of survival. New discoveries in our day are largely mental, instead of geographical, and the old battles of conquest have become wars with ignorance. They are struggles to overcome inefficiencies, attempts to broaden the common mental horizon, as our ancestors broadened their physical horizon. Very few people realize the rapidity with which technical advances are being made. Few realize how the way of this advance has itself advanced. I might make this more clear by an illustration.

Consider for a moment the increasing uses of chemical elements and compounds. New combinations in alloys, medicines, dyes, foods, etc., etc., and new uses and materials are being produced daily. For a more simple comparison, consider only the advances in our technical uses of the metallic chemical elements.

Copper, iron and five other metals were known and used at the time of Christ. In the first 1800 or 1900 years of our era, there were added to the list of metals in technical use (pure or alloyed) about eight more, less than two per century. There has been so much industrial advance made within the past twenty to thirty years that fourteen new metals have been brought into commercial use within this period. This is almost as many in our quarter-century as in the total preceding age of the world. Of course this rate, as applied to metals, apparently cannot continue, but there is no reason to question the possibility of the general advance it indicates. For centuries a single metal was made to serve for all uses which that metal could fill. Then two metals divided the field, each being used where it was preferred for any reason. Alloys began to displace metals to a limited extent. While the engineer still uses iron for his railroad, iron for his buildings and iron for his tools, these irons are different and have been specially developed for those uses. The electrical engineer prefers copper for his conductor,

certain irons for the frames of apparatus, other special irons and steels for the shafts, the magnetic fields, etc., and the specialization to best meet specific wants is still under way. I suppose that this kind of complex development is largely responsible for research laboratories.

A research laboratory is a place where men are especially occupied with new problems, presumably not too far in advance of technical application. By this group devoting its entire attention to the difficulties of meeting already well-defined necessities, or of newly defining and meeting together, the efficiency of those processes is increased. Men specially trained for this very purpose are employed and they are usually just as unfitted for successfully manufacturing as those who efficiently reproduce are of discovering or inventing. It is merely an extension of the principle of the maximum efficiency. A man with his entire attention devoted for months or years at a time to the difficulties of a single problem should be better able to reach a solution than the man who can devote only irregular intervals to it. He should then also be the better prepared for a second problem.

A research laboratory is also a place equipped with apparatus especially designed for experimental work. In a busy manufacturing plant, if a foreman has an idea pointing towards an improvement of his product he frequently has great difficulty in finding the time, the necessary idle apparatus, the raw materials and the incentive to try it. In the laboratory all of these are combined and there is added a system of coöperation of permanently recording results and an atmosphere of research.

The mathematics of coöperation of men and tools is interesting in this connection. Separated men trying their individual experiments contribute in proportion to their numbers, and their work may be called mathematically additive. The effect of a single piece of apparatus given to one man is also additive only, but when a group of men are coöperating, as distinct from merely operating, their work raises with some higher power of the number than the first power. It approaches the square for two men and the cube for three. Two men coöperating with two different and special pieces of apparatus, say a special furnace and a pyrometer, or an hydraulic press and new chemical substances, are more powerful than their arithmetical sum. These facts doubtless assist as assets of a research laboratory.

When a central organization, such as a laboratory, has access to all parts of a large manufacturing plant and is forced sooner or later to come into contact with the various processes and problems, the various possibilities and appliances, it can hardly fail to apply, in some degree, the above law of powers.

As a possible means of illustrating the almost certain assistance which one part of a manufacturing plant may give another when they are connected by experimenting departments or research laboratories and how one thread of work starts another, I will briefly review part of a single fairly connected line of work in our laboratory. In 1901 the Meter Depart-

¹ Presented before the Congress of Technology at the Fiftieth Anniversary of the Granting of the Charter of the Massachusetts Institute of Technology.

ment wanted electrically conducting rods of a million ohms resistance. These were to be one-quarter inch diameter by one inch length. In connection with this work we had to become fairly familiar with published attempts at making any type of such high resistances. Some kind of porcelain body containing a very little conducting material seemed a fair starting formula after the resistance of almost all kinds of materials had been considered. Our own porcelain department was of great help in showing us how to get a good start. We learned how and what to mix to get a fair porcelain, and we found that small quantities of carborundum or of graphite would give us the desired resistance about once in a hundred trials. The rods could be made, but the difference in their resistance when taken from the porcelain kiln and when they were made as nearly alike as we could make them, was often so many thousand-fold that something new had to be done to make a practical success. A small electric furnace was then devised for baking the rods and this was so arranged that the rate of rise of temperature, the maximum temperature reached and the duration of heat at any temperature was under control and was also recorded. The desired result was obtained and this work was thus finished. It gave us a certain stock of knowledge and assurance.

At that time a very similar problem was bothering one of the engineering departments. Lightning arrester rods, part of the apparatus for protecting power lines from lightning, were needed. Their dimensions were $\frac{3}{4} \times 6$ " and they needed to have a definite but, in this case, low resistance, and could apparently not be baked in a porcelain kiln. The usual temperature variations in such a kiln are so great that in practice many thousand rods were repeatedly fired and afterward tested to yield a few hundred of satisfactory product. All the cost of making an entire batch would have to be charged against the few units which might be found satisfactory, and in many cases there were none good in a thousand tested. It was evident that regulation and control of temperature was necessary. This was found to be impracticable in case any considerable number were to be fired at one time, as the heated mass was so great that the rods near the walls of the retort received a very different heat-treatment from those near the middle and were consequently electrically different. This was still the case even when electrically heated muffles were used. This difficulty led to experiments along the line of a heated pipe, through which the rods could be automatically passed. Some time was spent in trying to make a practical furnace out of a length of ordinary iron pipe, which was so arranged as to carry enough electric current to be heated to the proper baking temperature. Troubles here with oxidation of the iron finally led to substitution of carbon pipes. This resulted in a carbon tube furnace, which is merely a collection of six-foot carbon pipes, embedded in coke powder to prevent combustion, and held at the ends in water-cooled copper clamps, which introduce the electric current. By control of this current the temperature could be kept constant at any point desired. When this was combined with a constant rate of mechanical feed of

the air-dried rods of porcelain mixture, a good product was obtained. For the past seven years this furnace has turned out all the arrester rods, the number produced the last year being over 100,000 units.

In this work we were also forced to get into close touch with the electroplating department. The rods had to be copper-plated at the ends, to insure good electrical contact. The simple plating was not enough. This introduced other problems, which I will pass over, as I wish to follow the line of continuous experiment brought about, in part, at least, by the single investigation. The electric furnace consisting of the carbon tube packed in coke was a good tool for other work, and among other things we heated the carbon filaments for incandescent lamps in it. We were actuated by a theory that the high temperature thus obtainable would benefit the filament by removal of ash ingredients, which we knew the ordinary firing methods left there. While these were removed, the results did not prove the correctness of the theory, but rather the usefulness of trying experiments. It was found by experiment that the graphite coat on the ordinary lamp filament was so completely changed as to permit of a hundred per cent. increase in the lamp life or over 20 per cent. increase in the efficiency of the lamp for the same life, so that for the past four or five years a large part of the carbon lamps made in this country have been of this improved type. This is the Metallized, or "Gem" lamp. Naturally, this work started a great deal of other work along the lines of incandescent lamp improvement. At no time has such work been stopped, but in addition to it, the new lines of metallic filament lamps were taken up. In fact, during the past five or six years, a very large proportion of our entire work has been done along the line of metallic tungsten incandescent lamps. In this way we have been able to keep in the van of this line of manufacture. The carbon tube furnace has been elaborated for other purposes, so as to cover the action under high pressures and *in vacuo*. Particularly in the latter case a great deal of experimental work has been carried out, contributing to work such as that connected with rare metals. In such a furnace, materials which would react with gases have been studied to advantage. Our experience with the metallized graphite led to production of a special carbon for contact surfaces in railway signal devices, where ordinary carbon was inferior, and suggested the possibility of our contributing to improvements in carbon motor and generator brushes. On the basis of our previous experience and by using the usual factory methods, we became acquainted with the difficulties in producing carbon and graphite motor brushes with the reliability and regularity demanded by the motor art. Furnace-firing was a prime difficulty. Here again we resorted to special electrically heated muffles, where the temperatures, even below redness, could be carefully controlled and automatically recorded. This care, aided by much experimentation along the line of composition, of proportionality between the several kinds of carbon in the brush, etc., put us into shape to make really superior brushes. The Company has now been manufacturing these for a couple of years, with especial reference to particularly severe

requirements, such as railway motors. In such cases the question of selling price is so secondary that we can and do charge liberally for delicacy and care of operation in the manufacture.

This carbon work naturally led to other applications of the identical processes or materials. Circuit breakers, for example, are now equipped with a specially hard carbon contact, made somewhat as motor brushes are made.

It is not my intention to connect all of the laboratory work to the thread which seemed to connect these particular pieces of work, but rather to show the possible effect in accumulating in a laboratory experiences which might affect an inventory.

Among other considerations which appeal to me is one which may be worth pointing out. Probably almost every manufacturing plant develops among its workmen, from time to time, men who are particularly endowed with aptitude for research in their line. They are usually the inventors of the company. They are often discoverers in spite of opposition. They are always trying new things. They are almost of necessity somewhat inefficient in the routine production. In many plants they are merely endured, in a few they are encouraged. To my mind their proper utilization is a safe investment. A research laboratory assists in such a scheme. Sooner or later such a laboratory becomes acquainted with this type of men in a plant and helps them in the development of their ideas.

It is not a perfectly simple matter to measure the value of a research laboratory at any one time. In the minds of some, the proper estimate is based on the profit already earned through its work, which otherwise would not have been earned by the company. This is a fair and conservative method which in our generation ought to be satisfactory when applied not too early to the laboratories. It does not take into account what we may call the good-will and inventory value, both of which should be more rapidly augmenting than any other part of a plant. The experience and knowledge accumulated in a general research laboratory is a positive quantity. In our own case we expended in the first year not far from \$10,000, and had little more than expectations to show for it. Our expenses rapidly rose and our tangible assets began to accrue. Perhaps I can point to no better criterion of the value of a research laboratory to our company than the fact that its force was rapidly increased by a company which cannot be particularly interested in purely academic work. Our annual expenditures passed the \$100,000 mark several years ago. My own estimate of the value would probably be greater than that of others, for I am firmly convinced that proper scientific research is practically required by the existing conditions of our technical age.

Without going into exact values, which are always difficult to determine, consider for a moment the changes which incandescent lighting has witnessed in the past ten years. In this field our laboratory has been active, contributing to both carbon and to metallic filaments. Moreover, all of the improvements in this field have been the product of research laboratories of trained

men. In the case of our metallized carbon filament, which has now been in use several years, the efficiency of the light was increased by about twenty per cent. Among the carbon lamps of last year these were sold to the extent of over a million dollars.

A broader, but admittedly less accurate impression of changes recently produced may be gained by considering the economy now possible on the basis of our present incandescent lamp purchases in this country and that which would have resulted if the lamps of only ten years ago were used in their stead. On the assumption that the present rate of lamp consumption is equivalent to about eighty million 25-watt tungsten lamps per year, and on the basis of one and a quarter watts per candle power as against 3.1 of the earlier lamps and charging power at 10 cents per kilowatt hour, we get as a result a saving of \$240,000,000 per year, or $2\frac{2}{3}$ million per day. Naturally, this is a saving which is to be distributed among producers, consumers and others, but illustrates very well the possibilities. It is interesting to note that we are still very far removed from a perfect incandescent illuminant, when considered from the point of view of maximum theoretical light efficiency.

I see from advertisements that 65,000 of the Magnete arc lamps, originally a product of the laboratory, are now in use. These must have been sold for something near \$2,000,000. The supplying of electrodes which we make and which are consumed in these lamps should amount to about \$60,000 per year.

Our study of the properties of the mercury arc produced our rectifier, which has been commercially developed within the past few years. Of these, about 6,000 have been sold. As they sell for not far from \$200 per set, it is safe to say that this also represents a sale of over a million dollars. The advantage of these outfits over other available apparatus must also be recognized as not far from \$200 for each hour through which those already sold are all operating.

In such a complex field as insulations and molded materials there have been many changes produced. As far back as 1906 we were using annually, in a certain apparatus, 30,000 specially drilled and machined soapstone plates, which cost \$1.10 each. As the result of experiments on substitutes for such material, it was found that they could be molded by us in the proper shape, with holes in place and of a material giving increased toughness, at a greatly reduced cost. As the result of this fact, the price of the purchased material was reduced to us from \$1.10 to 60 cents which in itself would have paid for the work. But further developments proved that the new molded material could be made for 30 cents, which the foreign material could not equal, so we have since produced it ourselves. This caused a saving of approximately \$24,000 annually for this one molded piece. I have heard of other cases where prices to us have gone down, when we have obtained a little promise from our experimental researches.

In considering the research laboratory as a financial asset there is another view which might not be visible at first sight. It is the question of the difference between the value of the useful discovery when purchased

from competitors in the business and when made by one's own company. It is not usually pleasant to have to purchase inventions after their value is known, no matter from whom, but to have to pay a competitor for such a discovery is doubly irksome. One is naturally unduly fearful of its value to the competitor, and he, in turn, is overestimating another's power to use it. The purchaser's profit is apparently limited to the differences between his efficiency of operating it and that of the original owner.

I was recently informed by an officer of another large manufacturing company, where much chemical work is done and which established a research laboratory several years ago, that the most important values they got from their laboratory was the assurance that they were keeping ahead and are at least prepared for the new, if they cannot always invent it themselves. Incidentally, he said that from one part of their research work they had produced processes, etc., which had saved \$800,000 a year. They are at present spending in their several research departments a total of about \$300,000 a year.

We hear frequent reference to the German research laboratories, and a brief discussion may be in place. For the past fifty years that country has been advancing industrially beyond other countries. Not by new opened territories, new railroads, new farm lands, new water power cites, but by new technical discoveries. In fact, this advance may be said to be largely traceable to their *apparent* overproduction of research men by well-fitted universities and technical schools. Every year a few hundred new doctors of science and philosophy were thrown on the market. Most of them had been well trained to think and to experiment; to work hard, and to expect little. The chemical manufacturing began to be filled with this product and it overflowed into every other calling in Germany. These well-educated young men became the docents, the assistants and the professors of all the schools of the country. They worked for \$300 to \$500 per year. They were satisfied so long as they could experiment and study the laws of nature, because of the interest in these laws instilled into them by splendid teachers. This condition soon began to make itself manifest in the new making of things—all sorts of chemical compounds, all kinds of physical and electrical devices. I might say that pure organic chemistry at this time was academically most interesting. Its laws were entrancing to the enthusiastic chemist and consequently very many more doctors were turned out who wrote organic theses than any other kind. What more natural than that organic chemistry should have been the first to feel the stimulus? Hundreds, and even thousands of new commercial organic products are to be credited to these men and to that time. All the modern dyestuffs are in this class. Did Germany alone possess the raw material for this line? No! England and America had as much of that. But Germany had the *prepared men* and made the start.

It seems to me that America has made a start in preparing men for the research work of its industries. For example, it is no longer necessary to go abroad to

get the particular training in physical chemistry and electrochemistry which a few years ago was considered desirable. Advanced teaching of science is little, if any, more advanced in Germany to-day than it is in this country. In my opinion the quality of our research laboratories will improve as the supply of home-trained men increases, and that the laboratories of this kind will be increasingly valuable when analyzed as financial assets. I am certain, too, that the industries will not be slow in recognizing the growing value of such assets. They merely want to be shown.

Probably in most industries there are what I may call spots particularly vulnerable to research. For example, the efficiency of steam boilers, based upon the heat energy of the coal used and the efficiency of the engine using the steam, are continually being raised. We may expect, until the maximum calculable efficiency is reached, that this advance will continue. The reason is not far to seek. It is a vulnerable spot. Improvement is possible. A small increase in efficiency of power plant is an ever-continuing profit. Great numbers of steam power plants exist and so inventors are influenced by the fact that new improvements may result in enormous total economies. Every rule of the game encourages them. I can make this clearer by illustrations.

Artificial light is still produced at frightfully poor efficiency. Electric light from incandescent lamps has been greatly improved in this respect, but there is still room for greater economies. It is still a vulnerable spot.

In the case of iron used in transformers, we have another such vulnerable spot. A transformer is practically a mass of sheet iron, wound about with copper wire. The current must be carried around the iron a certain number of times and the copper is chosen because it does the work most economically. No more suitable material than copper seems immediately probable, nor is there any very promising way of increasing its efficiency, but in the iron about which it is wound there is a vulnerable spot. The size of the iron about which the copper is wound may possibly be still much further reducible by improvements in its quality. In other words, we do not yet know what determines the magnetic permeability or the hysteresis of the iron, and yet we do know that it has been greatly improved in the past few years and that it can still be greatly improved.

Let us make this vulnerable point a little clearer by considering the conditions here in Boston. I assume there are approximately 50,000 kilowatts of alternating current energy used here. Nearly all of this is subject to the losses of transformers. If the transformers used with this system were made more than ten years ago, they probably involve a total loss, due to eddy and hysteresis, of about \$1000 per day, at the ten-cent rate. Transformers as they are made to-day, by using improved iron, are saving nearly half of this loss, but there still remains over \$500 loss per day, to serve as a subject for interesting research work.

It should also be noted that Boston uses only a very

small fraction of the alternating current energy of this country.

Consider for a moment two references to the sciences and industry in Germany and England. Dr. O. N. Witt, professor in the Berlin Royal Technical High School, reporting to the German government in 1903, says: "What appears to me to be of far greater importance to the German chemical industry than its predominant appearance at the Columbian World's Fair, is the fact which finds expression in the German exhibits alone, that industry and science stand on the footing of mutual deepest appreciation, one ever influencing the other," etc. As against this, Prof. H. E. Armstrong, of entirely corresponding prominence and position in England, says of England: "Our policy is the precise reverse of that followed in Germany. Our manufacturers generally do not know what the word research means. They place their business under the control of practical men, who, as a rule, actu-

ally resent the introduction into the work of the scientifically trained assistants. If the English nation is to do even its fair share of the work of the world in the future, its attitude must be entirely changed. It must realize that steam and electricity have brought about a complete revolution, that the application of scientific principles and methods is becoming so universal elsewhere that all here who wish to succeed must adopt them."

So long as motors burn out, so long as subways are tied up by defective apparatus, so long as electric motors can run too hot, so long as street cars may catch fire from so-called explosions of the current, so long as the traffic of a whole city can be stopped by a defective insulation or a ten-cent motor brush, there will probably be the equivalent of research laboratories somewhere connected with the electrical industries, where attempts will be continually made to improve.

SCIENTIFIC SOCIETIES

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

THIRD SEMI-ANNUAL MEETING.

JUNE 21ST TO 24TH, 1911.

CONGRESS HOTEL, CHICAGO.

PROGRAM.

WEDNESDAY, JUNE 21ST.

Meeting at Congress Hotel, 10.00 A.M.

Address of Welcome.

Business Session.

Reports of Officers and Council.

Reports of Committees.

Special Report of Committee on Chemical Engineering Education: Dr. Samuel P. Sadtler, *Chairman*.

Discussions by several Professors of Chemical Engineering.

Luncheon.

Excursion, 1.30 P.M.

Visit to Plant of Swift & Company, Union Stock Yards.

EVENING SESSION.

Held at Armour Institute, 8.00 P.M.

Address of President Frerichs: "Method of Attacking Chemical Industrial Problems." (Illustrated by drawings and photographs.)

THURSDAY, JUNE 22ND.

Visit to Glucose Works at Argo, Ill., 9.30 A.M.

Luncheon at Congress Hotel.

Automobile Sight-seeing Trip, 3.00 P.M.

Subscription Dinner at Congress Hotel, 7.30 P.M.

FRIDAY, JUNE 23RD.

Session at Congress Hotel, 9.30 A.M.

Reading of Papers.

"Industrial Chemical Calculations, by Professor Joseph W. Richards.

"Rapid Determination of Tin in Food Products," by Edward G. Gudeman.

"Distillation on the Continuous System," by Charles L. Campbell.

"A New System of Lead and Silver Lining," by Charles L. Campbell.

"The Institute and the U. S. Patent System," by William M. Grosvenor.

Luncheon.

Excursions (Alternative), 1.00 P.M.

Carter White Lead Company, West Pullman.

Semet-Solvay Coke Ovens of the By-Products Coke Corporation, 112th St. and Torrance, South Chicago.

Evening Session at Congress Hotel, 7.30 P.M.

"Manufacture of Gelatine," by Ludwig A. Thiele.

"The Practical Value of Calorific Tests on Anthracite Coal," and "Two Methods of Testing Asphalt," by S. F. Peckham.

Final Business Session.

SATURDAY, JUNE 24TH.

Excursions: Gary Plant of the Indiana Steel Company, Gary, Ind.; Universal Portland Cement Co., Buffington, Ind.

Permits have also been obtained to visit the Illinois Steel Company Works, South Chicago, where eleven blast-furnaces are in operation, besides open-hearth, Bessemer and open-hearth by an electric process. A portion of the furnaces are supplied with dry-air blast. There are large rolling mills for all varieties of structural steel. Standard Oil Refinery at Whiting, Indiana.

Adjournment.

Local Committee of Arrangements:

A. Bement, *Chairman*, 206 So. La Salle St., Chicago.

P. C. Brooks, *Secretary and Treasurer*, Hegewisch, Ill., Oscar Linder, T. G. Wagner.

J. C. OLSEN, *Secretary*,

Polytechnic Institute,

Brooklyn, N. Y.

AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS.

The Annual Convention of the American Institute of Electrical Engineers, for 1911, will be held in

Chicago, Ill., on Monday to Friday, June 26, to 30, 1911. The Institute headquarters will be at the New Hotel Sherman, northwest corner of Clark and Randolph streets. There will be a reception on Monday evening, and the technical sessions will open on Tuesday morning. The Convention Committee will have charge of the local arrangements. The members of this committee are as follows: Louis A. Ferguson, *Chairman*; W. L. Abbott; B. J. Arnold; H. M. Byllesby; W. Lee Campbell; T. P. Gaylord; William B. Jackson; J. W. Johnson; John D. Nies; W. P. Sidley; B. E. Sunny; Fay Woodmansee; P. B. Woodworth; J. G. Wray.

It is many years since the annual convention was held in Chicago, and the committees are arranging to make it both profitable and interesting to the members and their guests.

The following is a partial list of the papers that will be presented:

PROGRAM.

"Economical Design of Direct-Current Magnets," by R. Wikander.

"Catenary Span Calculations," by W. L. R. Robertson.

"Currents in Inductors of Induction Motors," by H. Wiechsel.

"Multiplex Telephony and Telegraphy by Means of Electric Waves Guided by Wires," by Major G. O. Squier.

"Electrolysis in Reinforced Concrete," by C. E. Magnusson and G. H. Smith.

"Induction Motor Design," by T. Hook.

"The High Efficiency Suspension Insulators," by A. O. Austin.

"The Electric Strength of Air II," by J. B. Whitehead.

"Electrification Analyzed, and Its Application to Trunk Line Roads," by W. S. Murray. (Abstract of paper presented before Institute meeting at Toronto on April 7.)

"Telegraph Transmission," by F. F. Fowle.

"The Cost of Transformer Losses," by R. W. Atkinson and C. E. Stone.

"The Costs of Railway Electrification," by B. F. Wood.

"Induction Motor for Single-Phase Traction," by E. F. W. Alexanderson.

"Magnetic Properties of Iron at 200,000 Cycles," by E. F. W. Alexanderson.

"Electric Storage Batteries," by Bruce Ford.

"The Characteristics of Isolated Plants," by P. R. Moses.

"Elevator Control," by T. E. Barnum.

"Limits to the Use of Resistance Materials."

Two papers on educational topics.

Some of these papers are printed in the current issue of the Proceedings. The others will appear in the June and July issues. Full details regarding the convention, including the program and transportation arrangements, will be published in the June Proceedings.

AMERICAN CHEMICAL SOCIETY.

INDIANAPOLIS MEETING.

The forty-fourth annual meeting of the American Chemical Society will be held in Indianapolis, Indiana, June 28th to July 1st, inclusive. A meeting of the Council will be held at 2.30 P.M. on Tuesday, June 27th.

Hotel headquarters will be the Claypool Hotel, but the meetings themselves will all be held at the German House, which is not a hotel but a German club house. The smoker will be held at the German House, where lunches will also be served. The building is one of the most suitable in Indianapolis and has been leased for the occasion. The fact that it has the atmosphere of a club will add very greatly to the attractiveness of the meeting.

The Indiana Section is making a special effort to entertain the members, and the outlook at present is for one of the largest and most successful meetings the Society has ever held.

Mr. Harry E. Barnard, of the Indiana State Board of Health, is chairman of the Local Committee and Mr. H. A. Schwarz, 522 Tibbs Ave., Indianapolis, is chairman of the Local Publicity Committee. Either one of these gentlemen will be glad to place himself at the disposal of any of the members of the Society to give them information as to local conditions and the special attractions of the meeting itself.

The Entertainment Committee is planning an interesting program, which will be an undoubted success, and special attention is being paid to preparations for the entertainment of ladies at such times as they cannot participate in the regular program. Many manufacturing plants will be visited and many papers of importance read.

The following is a rough draft of the program, which will undoubtedly be changed to meet new conditions that may arise.

WEDNESDAY, JUNE 28TH.

Morning—General meeting.

Afternoon—Division meetings.

Evening—Smoker.

THURSDAY, JUNE 29TH.

Morning—Division meetings.

Afternoon—Visit to Eli Lilly Co., where the Pharmaceutical Division will hold a meeting and assist in dedicating the new laboratories.

Evening—Automobile ride to the Country Club: luncheon, lawn fete, dancing, music, etc.

FRIDAY, JUNE 30TH.

Morning—Division meeting.

Afternoon—Visit to manufacturing plants.

Evening—Banquet.

SATURDAY, JULY 1ST.

Morning—Unfinished division meetings and visit to plants.

Afternoon—Unfinished division meetings and visit to plants.

INTERNATIONAL CONGRESS.

President Taft has appointed the following as the official representatives of the respective bureaus of the federal government on the Organizing Committee

of the International Congress of Applied Chemistry: *Department of the Treasury*—Dr. Reid Hunt, Hygienic Laboratory, Marine Hospital Service; Dr. A. B. Adams, Internal Revenue Service. *Department of the Interior*—Mr. George Steiger, Geological Survey; Dr. George S. Ely, Patent Office; Professor Nathaniel W. Lord, Ohio State University, Columbus, O., to represent Bureau of Mines. *Department of Agriculture*—Dr. H. W. Wiley, Chief, Bureau of Chemistry; Dr. C. F. Langworthy, Office of Experiment Stations; Professor W. W. Cooke, Biological Survey; Mr. William L. Hall, Forest Service; Dr. Frank E. Cameron, Bureau of Soils; Professor W. J. Humphreys, Weather Bureau; Dr. R. H. True, Bureau of Plant Industry; Dr. Marion Dorset, Bureau of Animal Industry; Dr. W. F. Hillebrand, Chief Chemist, Bureau of Standards.

The Pennsylvania Legislature has passed a concurrent resolution, providing for the appointment of a chemist to officially represent the Commonwealth of Pennsylvania at the Eighth International Congress.

The Preliminary Announcement, dated March 6, 1911, has been translated into French under the auspices of the Association des Chimistes du Sucrierie et de Distillerie; into German under the auspices of the Verein Deutscher Chemiker; and into Italian under the auspices of the Instituto Chimico and is being distributed by these societies. The Society of Chemical Industry has undertaken to distribute the Announcement to all the chemists of the British Empire.

A pamphlet addressed specifically to American manufacturers, showing them how their business interests may be benefited by coöperation with the Congress, is in preparation and will be ready for distribution by the middle of May.

Under the leadership of the Verein Deutscher Chemiker, ten technical societies have already begun

an organization for Germany along the lines of the American organization for the Congress; in England, the Society of Chemical Industry has taken the initiative along similar lines.

SOCIETY FOR ENGINEERING EDUCATION.

The nineteenth annual meeting of the Society for the Promotion of Engineering Education will be held at Pittsburg, Pa., on Tuesday, Wednesday and Thursday, June 27th, 28th and 29th. The headquarters will be at the Carnegie Technical Schools.

At the meeting special attention will be given to the reports of the Committees on the Teaching of Mathematics to Engineering Students and to Entrance Examinations for Technical Schools.

Particulars regarding the meeting can be obtained from Professor H. H. Norris, Cornell University, Ithaca, N. Y.

SOCIETY CHEMICAL INDUSTRY.

ANNUAL GENERAL MEETING, 1911.

The annual General Meeting will be held in the Montgomery Hall, Sheffield, at 10.30 A.M., on Wednesday, July 12, 1911. A program of the proceedings will be issued later.

MEETING OF SOUTHERN ASSOCIATION.

The annual meeting of the Southern Fertilizer Association will be held at Atlantic City, N. J., July 17, 1911. Already there are indications of a very large attendance of the members of this organization.

An Academy for Silk Industry is being erected in Nagana, Japan, and an Academy for Mining and Metallurgy in Akita.

EDUCATIONAL

PRATT INSTITUTE EXHIBIT.

The annual exhibition of the students of Pratt Institute was held on June 1st, 2nd and 3rd in the buildings of the Institute in Brooklyn.

In the School of Science and Technology, which is the division of the Institute especially concerned with the training of young men in industrial and technical lines, the various classes were at work in the shops and laboratories during the exhibit, and thus an excellent opportunity was given those interested to inspect not only the results of the students' work, but also the methods of instruction and the general facilities for conducting this kind of training.

A special feature of the exhibition was the opening of the new tannery of the Institute, recently installed to provide for the courses in Tanning and Leather

Chemistry which are to be conducted in co-operation with the National Association of Tanners.

On May 5th, New York University celebrated the 100th anniversary of the birth of John William Draper who was professor of chemistry in New York University. Dr. John J. Stevenson, emeritus professor of geology, presided and gave a short résumé of Draper's life and work. Dr. Arthur B. Lamb, director of the chemical department, exhibited some of Dr. Draper's original instruments which were used in producing the first daguerreotypes.

In the near future the New York Section of the American Chemical Society will have a celebration befitting the importance of Draper's work.

Harvard University has raised the \$50,000 necessary to complete the \$100,000 Wolcott Gibbs Memorial Laboratory Fund which was started by Dr. Morris Loeb and Mr. James Loeb, of New York, by a donation of \$50,000. It is expected that \$65,000 will be expended on the construction and \$35,000 on the maintenance of the building.

Professor Julius O. Stieglitz, of the University of Chicago, and Professor B. B. Boltwood, of Yale University, have been elected to membership in the National Academy of Sciences, and Professor Ernest Rutherford, of the University of Manchester, has been elected a foreign associate.

Miss Caroline L. Hunt (32 Eliot St., Jamaica Plain, Mass.) is preparing a life of the late Prof. Mrs. Ellen H. Richards and will appreciate receiving any material such as letters, photographs, etc., which might be of assistance in preparing the biography.

On April 4th, Professor Coblenz formally resigned his chair as Professor of General Chemistry in the New York College of Pharmacy, which he has occupied for many years, to assume the duties of a new position with the firm of E. R. Squibb & Sons.

Dr. F. W. Woll, Professor of Agricultural Chemistry at the University of Wisconsin, will represent the

University at the Centennial celebration of the University of Christiania, Norway, in September.

Harry J. Sears and Alice R. Berger have been appointed instructors in chemistry at Stanford University, and Dr. Robert E. Swain has been promoted to be professor of physiological chemistry.

Dr. J. W. Turrentine, instructor in physical and electrochemistry at Wesleyan University, has been appointed scientist in the laboratory of the Bureau of Soils, U. S. Dept. of Agriculture.

The Bessemer gold medal of the Iron and Steel Institute of London for this year will be awarded to Prof. Henri Le Chatelier, the French metallurgist.

The University of Edinburgh will confer its doctorate of laws on Prof. Ernest Rutherford, of the University of Manchester.

Dr. Elmer Ellsworth Brown, U. S. Commissioner of Education, has been elected chancellor of New York University.

Prof. William A. Noyes has been elected President of the Illinois State Academy of Science.

NOTES AND CORRESPONDENCE.

THE INVENTOR OF CELLULOID.

In a recent review¹ of a work on celluloid, the statement appears that "it is not surprising that there should be some mistakes, errors, and omissions. In the first chapter, the invention of celluloid which belongs to Daniel Spill, of Hackney, England, is credited to Hyatt," the inference being that Spill and not Hyatt was the inventor of celluloid. This is not a question of the expression of individual opinion—to which all are entitled—for the statement that the invention of celluloid belongs to Spill is an error of *fact*, readily disproved by historical data, which data, in the interests of accuracy, is appended herewith.

As the result of conversations with his friend John Taylor, who patented the manufacture of cellulose nitrates in England (Eng. Pat. 11,407, 1846) for Schönbein, who is credited with their discovery, Alexander Parkes began experiments with pyroxylin in Birmingham at the laboratory of Elkington, Mason & Co., where he was then employed, which experiments resulted in there being granted to him E. P., 2,359, 1855. This was followed by E. P. 1,123, 1,125, 1856, and later by E. P. 2,675, 1864; 1,313, 2,733, 3,163, 1865; 1,564, 1,592, 2,709, 1866; 865, 1,695,

1867; 1,366, 1,614, 1868; 983, 1881; F. P. 71,871, 1866, all of which contained pyroxylin. His product—to which the name Parkesine was given—in its more successful forms comprised pyroxylin, camphor and alcohol, with and without vegetable oils, and is fully described in *Jour. Soc. Arts*, 1865, No. 683, Dec. 15, p. 81, and by Lewthwaite in his process for "Coating Fabrics with Parkesine" (E. P. 741, 1868; U. S. P. 103,209, 1870). After Parkes' Company suspended operations in 1867, the first patent (E. P. 1,816, 1867) of Daniel Spill, appeared, which he followed by others (E. P. 2,6661 1867; 3,984, 1868; 3,102, 1869; 180, 787, 1,017, 1,626, 2,649, 1870; 1,739, 1875; F. P. 85,369, 1869; 88,898, 1870). Spill gave to his product one name only, *i. e.*, Xylonite, or Cotton Xyloidine, taking the name "xyloidine" from Braconnet's term for the nitrated starch discovered and described by him in 1833.² His last process was patented in 1875 (E. P. 1,739), and two years later the British Xylonite Company was formed, taking its name from the word "Xylonite" which Spill originated to designate his product. After Spill had been granted his four United States patents (91,377, 91,378, 97,454, 1869; 101,175, 1870) the U. S. branch chose a name as near xylonite as possible without infringing on the parent name,

¹ THIS JOURNAL, 3, 194 (1911)

² *Ann. chim. phys.*, 52, 290 (1833); *Pogg. Ann.*, 29, 176 (1833).

namely zylonite. The writer has read in detail all the testimony of all the suits in which the American Zylonite Co. participated, in none of which is claim laid to the use of the word "celluloid."

In 1863, John Wesley Hyatt was a printer in Albany, New York, and hearing of a prize of ten thousand dollars offered by Phelan & Collender, a New York City firm, for the patent rights for a satisfactory process for the manufacture of a billiard ball containing no ivory, began experiments in billiard ball manufacture. Mr. Hyatt told the writer, in 1910, that, until required by his attorneys to modify certain claims in his then pending U. S. P., 91,341, 1869, he had not heard of the work with pyroxylin of Parkes, Spill, Berard (E. P. 607, 1856; 1,883, 1,884, 1857), Thistlewaite (E. P. 1,159 1856), MacIntosh and Rhodes (E. P. 734, 1859), Barnwell and Rollason (E. P. 945, 1859; 2,249, 1860), Mennons (E. P. 2,775, 1860), Henry (E. P. 1,454, 1860), Cartright (E. P. 365, 1863), Cutting (E. P. 1,636, 1854), Pierson (U. S. P. 65,267, 1867), Seely (U. S. P. 79,261, 1868), Kendall and Trested (U. S. P. 86,841, 1869) or others in the pyroxylin patent field. J. Hyatt started out by applying to the problem certain principles of heat and great pressure, fully described in his earlier U. S. Patents (31,461, 1861; 35,652, 1862; 50,359, 1865; 76,765, 1868; 88,633, 88,634, 89,582, 91,233, 91,234, 91,235, 1869). His experiments reached such a stage of success that he called his brother Isaiah Smith Hyatt, then an editor at Rockford, Ill., and the latter in Albany in 1868 or the early part of 1869, gave to the product the name celluloid, from "cellulose" and "oid" meaning "like," this being the origin of the word. The word celluloid, as expressing a distinct product, was therefore the invention of the Hyatts, and the product was first made by them at the factory of Osborn, Newcomb & Co., on Eagle St., Albany, N. Y. This firm name was soon changed to the Hyatt Manufacturing Co., then to the Albany Billiard Ball Co., the firm under the latter name being in active existence in Albany to-day. Just as the company formed to exploit Spill's English xylonite patents was named the British Xylonite Co., and to work his U. S. patents of zylonite was known as the American Zylonite Co., so the firm organized to manufacture celluloid was termed the Celluloid Co. Celluloid as a name was registered as a trade mark in the United States Patent Office Jan. 14, 1873, as No. 1,102, and again in 1883.

When the Cellonite Manufacturing Company was restrained from the use of the word "cellonite" because it sounded so much like celluloid (U. S. Circuit Court—District of New Jersey, decided July 12, 1887; Patent Office Gazette, Vol. 41, Nov. 8, 1887, p. 693) Judge J. Bradley in handing down the decision stated: "The word 'Celluloid' had never been used before, except . . . by Isaiah S. and John W. Hyatt, by whom the word was coined," and "that the word 'Cellonite' is sufficiently like it to produce the mischief which is within the purview of the law."

Spill was not even the first to describe the use of camphor and alcohol with pyroxylin—the combination which induces plasticity. While it is true that

Spill brought suit in the United States to restrain certain manufacturers from the use of an ethyl alcohol solution of camphor, and came personally to the United States to prosecute those suits and won; and while it is also true that Spill sued again to restrain the same company from the use of a methyl alcohol solution of camphor, it is also true that the second suit was lost to Spill on the ground that Parkes in his patents above quoted, and not Spill, was the pioneer in the use of camphor in alcohols as solvents for the cellulose nitrates. The second suit being lost, the first decision was appealed and reversed, all of which is given in detail in 22 Blatchford C. C. R. 441.

In all the works on celluloid of which the writer is aware, and specifically Joseph Ertel, p. 9; Fr. Böckmann, p. 2; L. Andes, p. 10; and Masselon, Roberts and Cillard, p. 2, the statement occurs that celluloid was discovered by the Hyatt Brothers in Newark, N. J. in 1869. As mentioned above, this statement is untrue in that the product was discovered in Albany, and Mr. John W. Hyatt informed the writer that he had never been to Newark until in the early seventies.

E. C. WOODRUFF

CELLULOID FROM ACETYLCELLULOSE.

Up to the present, acetylcellulose found application only as a varnish for coating objects where non-inflammability and certain electric properties were required. The main use was for the manufacture of cinematograph films, which did not burn even after ignition. Altogether, it has been impossible to make objects from it more than one-fourth of a millimeter in thickness.

Dr. A. Eichengrün has now discovered (*Zeitschrift für angewandte Chemie*, 1911, 366) a method of making celluloid of any shape, color and thickness, using acetylcellulose instead of nitrocellulose. In this manner, he has produced an incombustible substitute for celluloid which he calls "Cellon." His invention seems to be laid down in his French Patent 412,797 of January 20, 1910, and British Patent 1441 of January 19, 1910, the essence of which is:

"Certain types of cellulose acetate, notably these which are soluble in acetone, are soluble on heating, in mixtures of liquids, *e. g.*, methyl alcohol and benzene, neither of which have any solvent action alone. On cooling these solutions, the ester may either remain in solution or separate out in the form of long felted filaments. The separation may be prevented by adding to the solution any of the ordinary solvents of cellulose acetate, in which it is soluble in the cold, *e. g.*, glacial acetic acid, acetone, etc., in which case the solution remains liquid or becomes syrupy on cooling. Or else, there may be added a substance having an influence analogous to that of camphor in nitrocellulose, in which case the solution sets to a continuous mass on cooling. Suitable bodies are methylacetanilide, ethyltoluenesulphonate, trichloraniline, etc. If a very concentrated mass be desired, the cellulose acetate may be dissolved in alcohol and benzene, freed from impurities by filtration and allowed to deposit by cooling; the liquid is then poured

off and the precipitated cellulose acetate worked up with a camphor substitute. One of the numerous examples of the process runs as follows: 1 kilo of cellulose acetate is dissolved in 2 kilos of methyl alcohol and 1 kilo of toluene at 80° C.; 150 grams of methyl-acetanilide are added to the solution and 100 grams of epichlorhydrin. The liquid is filtered hot and on cooling sets to a solid mass, which may be sliced, moulded, or pressed through orifices. In various ways plastic masses having all the technical properties of celluloid may be prepared."

SACCHARIN IN FOOD.

FOOD INSPECTION DECISION 135.

At the request of the Secretary of Agriculture, the Referee Board of Consulting Scientific Experts has conducted an investigation as to the effect on health of the use of saccharin. The investigation has been concluded, and the Referee Board reports that the continued use of saccharin for a long time in quantities over three-tenths of a gram per day is liable to impair digestion, and that the addition of saccharin as a substitute for cane sugar or other forms of sugar reduces the food value of the sweetened product and hence lowers its quality.

Saccharin has been used as a substitute for sugar in over thirty classes of foods in which sugar is commonly recognized as a normal and valuable ingredient. If the use of saccharin be continued it is evident that amounts of saccharin may readily be consumed which will, through continual use, produce digestive disturbances. In every food in which saccharin is used, some other sweetening agent known to be harmless to health can be substituted, and there is not even a pretense that saccharin is a necessity in the manufacture of food products. Under the Food and Drugs Act articles of food are adulterated if they contain added poisonous or other added deleterious ingredients which may render them injurious to health. Articles of food are also adulterated within the meaning of the act, if substances have been mixed and packed with the foods so as to reduce or lower or injuriously affect their quality or strength. The findings of the Referee Board show that saccharin in food is such an added poisonous or other added deleterious ingredient as is contemplated by the act, and also that the substitution of saccharin for sugar in foods reduces and lowers their quality.

The Secretary of Agriculture, therefore, will regard as adulterated under the Food and Drugs Act foods containing saccharin which, on and after July 1, 1911, are manufactured or offered for sale in the District of Columbia or the Territories, or shipped in interstate or foreign commerce, or offered for importation into the United States.

FRANKLIN MACVEAGH,

Secretary of the Treasury.

JAMES WILSON,

Secretary of Agriculture.

CHARLES NAGEL,

Sec. of Commerce and Labor.

WASHINGTON, D. C., April 26, 1911.

USE OF SACCHARIN.

The experiments of the Referee Board of Consulting Scientific Experts of the Department of Agriculture show that the continued use of saccharin for a long time in quantities of over $\frac{3}{10}$ of a grain is liable to impair digestion.

Considering that saccharin is 550 times as sweet as cane sugar, $\frac{3}{10}$ of a gram possesses the sweetening power of 165 grams of cane sugar. It is hardly conceivable that any one person would daily digest such an amount of saccharin in food and beverage, and without having studied in detail the experiments carried out by the scientists of the Referee Board, the conclusion seems to be justified that saccharin—as has been the case in Europe—has been sacrificed to the agrarian interests of the country. But in spite of all restrictions the consumption of saccharin for technical uses is enormous in Europe.

In Germany, for example, the production of artificial sweeteners and their importation has been forbidden by the law of July 7, 1902. The existing factories were bought out by the government and received an indemnity of about five million marks.

The price of cane sugar did not rise in consequence of this arbitrary removal of the dangerous competitor, but an immense amount of smuggling of saccharine from Switzerland and Belgium into Germany and Austria was the result. From April 1, 1904, to December, 1910, over 11,000 k. of saccharin were confiscated at the Swiss-Austrian border and 444 smugglers were arrested and convicted. Much larger quantities were of course surreptitiously brought into Germany, and a train running by night time from Switzerland into Germany is called the "Saccharin Train" because so many smugglers are traveling on it.

In Zurich alone there are 129 persons who make the smuggling of saccharin a specialty, and these people exercise the greatest ingenuity in concealing saccharin. In one case they hid in each of 30 barrels of herrings, which were to be forwarded across the frontier, a tin can containing 25 k. of the sweetener. Again, they filled champagne bottles with the material, and in another instance they packed tin tubes containing saccharin into cans in which sesame oil was shipped.

The sweetener thus marketed is employed by householders exclusively who refuse to believe that saccharin is injurious to health, and who prefer to use the sweetener on account of its sweetness.

The Editor of the Journal of Industrial and Engineering Chemistry:

With the enlargement of the policy of the JOURNAL and the effort of the Industrial Section of the American Chemical Society to be of greater value to its members as well as to the public at large, it might now be well to take into consideration one of the most vital points of interest, especially to the younger members, *i. e.*, the question of finding the particular line of employment for which each is suited.

I do not mean by this to refer to the man who is habitually out of a job but first to the young man who

is just starting out in life. He should have a better opportunity to make a selection than is, as a rule, offered. Secondly, there is the class, to which many ambitious young men belong, which consists of those who have positions which are not suited to their training or which they have outgrown and in which there is no further chance for advancement.

It appeals to many men, with whom I have discussed the subject, that, by acting as a clearing-house for members of the Society, who wish a change of employment and for the corporations, who wish to employ chemists, the Society would be serving a good cause and further the interests of the greater number of its members.

This problem is already solved, but to a very small extent, by the "want ads" which can be inserted in the *Journal of the American Chemical Society*.

The opportunity possessed by the Society is unique in that among its members are numbered those most prominent in each of the various fields of chemistry, and that any one of its members seeking employment can be vouched for by some one who is a specialist in his own line and who therefore knows the true value of the man. In this manner the recommendations should carry a weight which is not carried by other forms of recommendation and result in placing the right man in the right place a much greater number of times than is at present the case.

I am much interested in a plan of this nature and hope that it may be taken up officially by the Society as a whole. In the meantime I should like to hear from any one interested in any way whatsoever.

RAYMOND C. BENNER.

UNIVERSITY OF ARIZONA,
TUCSON.

WORLD-WIDE FIGURES.

Through study and observation of the volcanic outflow the geologist knows approximately the composition of the earth's crust to a depth of 10 miles below sea-level. As Frank W. Clarke, of the United States Geological Survey, says in the "Data of Geochemistry:" "This thickness of 10 miles represents known matter." The vastness of the figures which it is necessary to employ in the discussion of this 10-mile lithosphere, as it is termed, transcends ordinary human comprehension.

The volume of the lithosphere, including the continents elevated above the sea, is 1,633,000,000 cubic miles.

A cubic mile of average rock weighs 12,800,000,000 tons.

The volume of the ocean is 302,000,000 cubic miles.

The atmosphere is equal in weight to 1,268,000 cubic miles of water, which, however, is only one two-hundred-and-thirty-eighth of the volume of the ocean; yet this would be sufficient to raise the level of the ocean 45 feet on all shores and to submerge an important part of the continents.

One per cent. of the water of the ocean would cover all the land areas of the globe to a depth of 290 feet.

The salt in the ocean would make 4,800,000 cubes

each 1 mile in dimensions, which, if spread over the United States, would form a layer 1.6 miles high.

In comparison with this outer 10-mile section of the earth's crust, the thin sheet of organic matter on the surface—the prairie and valley soils, the alluvial bottoms, and the rich tablelands by whose products man lives—becomes a mere film, a skin.

CONDENSITE, A NEW ACID- AND ALKALI-PROOF PLASTIC MATERIAL.

Under this name, a new phenol-formaldehyde product is to be placed on the market, the properties of which are claimed to be superior to all similar substances heretofore introduced. Condensite is soluble in alcohol and can be employed like shellac for varnish purposes, etc.

By simple heating, Condensite is converted into the insoluble variety ready for use as a plastic material. It can be perfectly moulded, it sets rapidly without any air holes. Its electric properties are excellent. It possesses great tenacity, is tasteless and odorless.

The product is manufactured by the Condensite Company of America, in Glen Ridge, N. J., and is the invention of J. W. Aylsworth, who has spent a lifetime in Edison's laboratories as research chemist. Mr. Edison has reserved for himself the exclusive rights for using the new material for phonographic purposes. Mr. Frank L. Dyer, the attorney of the Edison interests, is the treasurer of the company and Mr. Kirk Brown its president. Mr. Aylsworth, the inventor, is a director in the company and will act as its consulting chemist.

AMERICAN TIN-PLATE INDUSTRY.

From information supplied by the Bureau of Statistics it appears that during the first eight months of the fiscal year 1911 both the tin imports and the tin-plate exports of the United States exceeded all previous records for a similar period. The total imports of pig tin, of which England and the Straits Settlements are the chief sources of supply, amounted in the eight months ending with February, 1911, to 68,000,000 pounds (compared with 66,500,000 pounds in the same months of the preceding fiscal period), valued at \$23,500,000, and will probably approximate in value \$35,000,000 for the full fiscal year. The exports of tin and terne plates in the eight elapsed months of the current fiscal year aggregated 24,250,000 pounds (in contrast to 15,000,000 pounds in the corresponding period of 1910), valued at \$880,000, and the total exportation for the complete fiscal year is estimated at \$1,333,000.

ALCOHOL FROM SAWDUST.

The problem of the utilization of sawdust for the conversion of cellulose into sugar and the subsequent production of alcohol by fermentation has been economically solved.

A plant established at Georgetown, S. C., has been

running successfully for over one year, producing more than 2,000 gallons of ethylic alcohol per day. The capacity of the plant is about 5,000 gallons daily.

The process carried out at Georgetown is founded on the Ewen-Tomlinson inventions which have been patented in all the civilized countries. The works in Georgetown are partly owned by the Du Pont Powder Co., and the alcohol there produced is used in their manufacture of powder.

ALABAMA COKE.

There were 43 coke-making establishments in Alabama in 1910, the same number as in 1909, but the total number of ovens increased from 10,061 in 1909 to 10,132 in 1910, exclusive of the 60 Koppers ovens under construction at the close of 1910. Of these, 9,614 ovens were in operation in 1910, with an average production of 338 short tons each. In 1909 the average production per oven was 330 tons.

The following table shows the growth of the coke-making industry in Alabama:

	Short tons.
1880.....	60,781
1890.....	1,072,942
1900.....	2,110,837
1905.....	2,576,986
1906.....	3,034,501
1907.....	3,021,794
1908.....	2,362,666
1909.....	3,085,824
1910.....	3,249,027

INCREASED LEAD PRODUCTION IN 1910.

The production of refined lead in the United States in 1910, as shown by an advance statement issued by the United States Geological Survey, was 470,380 tons, an increase over the figures for 1909 of 22,268 tons.

The following are the States which smelted or refined lead in excess of 10,000 tons:

	1909. Short tons.	1910. Short tons.
Missouri.....	142,650	161,659
Idaho.....	97,183	99,924
Utah.....	64,534	57,081
Colorado.....	29,326	35,685

GROWTH OF CEMENT INDUSTRY.

Few mineral products can show so rapid an increase in output as Portland cement. The production for 1909, according to the United States Geological Survey, was the greatest in the history of the industry, being 65,399,889 barrels, valued at \$52,797,973. In 1900 the production was only 17,231,150 barrels, in 1902 it was 25,753,504 barrels, in 1905 it was 31,675,257 barrels, in 1906 it was 51,000,445 barrels, and in 1908 it was 52,910,925 barrels.

PUMICE.

The value of the pumice produced in the United States in 1909 was \$33,439 and that of the pumice imported was nearly three times as great, according to the figures recently published by the United States

Geological Survey. The native supply comes principally from deposits in Harlan and Lincoln counties, Nebr. Pumice is an acidic volcanic rock, which may be in either massive or finely comminuted form.

ENDOWMENT COMMITTEE.

Mr. Hyde announces the completion of the organization of the Endowment Committee as follows:

B. T. Babbitt Hyde, Chairman, 11 Broadway, New York.

Arthur L. Day, Geophysical Laboratory, Carnegie Institute, Washington, D. C.

Wm. L. Dudley, Vanderbilt University, Nashville, Tenn.

A. D. Little, 93 Broad Street, Boston, Mass.

E. G. Love, 80 East 55th Street, New York.

Theo. B. Wagner, 746 Marquette Terrace, Chicago, Ill.

GENERAL NOTES.

The annual dinner of the Utah Society of Engineers was held at the Commercial Club, Salt Lake City, Thursday, April 20, 1911. Addresses were made by President John Dern, of the American Mining Congress, and by various members of the Society. The following officers were elected to serve for the year 1911-1912:

President, M. D. GROSH.

First Vice-President, C. F. MOORE.

Second Vice-President, E. H. BECKSTRAND.

Secretary, R. B. KETCHUM.

Treasurer, A. S. PETERS.

W. C. EBAUGH,

Secretary U. S. E.

Swift & Co., Chicago, are building a cottonseed oil refinery at Harvey, opposite New Orleans, La. The buildings, which are on the river front, located on a tract of 37 acres, are nearing completion, and include an oil refinery, 115 × 52 feet, brick and concrete construction, fireproof throughout, part of which is four and the other three stories high; the packing and shipping building, 128 × 61 feet, two stories high; cooper shop, 64 × 64 feet, two stories high; boiler and engine room, 79 × 40 feet.

The plant will be ready for operation about the middle of June, and will employ a large number of hands.

On April 13th, Prof. Wm. B. Alwood, enological chemist of the Bureau of Chemistry, U. S. Dept. of Agriculture, sailed for Spain to investigate viticultural conditions in Spain, France, Germany and Italy. While in Europe Dr. Alwood will read several papers on the chemistry of American grapes before the International Viticultural Congress when it meets at Montpellier.

The Union Phosphate Co., Union City, Ga., will

expend \$20,000 on improvements and additions to their buildings. The main building will be increased to 70 × 300 feet. When the additions are completed, the capacity will be 100 tons of acid phosphate daily. J. G. Eubanks is the president of the company, which has a capital stock of \$150,000.

Work has begun on the foundation of the new fertilizer plant, 114 × 135 feet, on the site purchased by the Central Chemical Co., Hagerstown, Md., in the northern suburbs along the Cumberland Valley Railway. The new plant when completed will have a capacity of 20,000 tons a year.

On April 28th, the Arbuckle Bros. Sugar Refinery in New York City was destroyed by fire causing a loss of about \$400,000. Nothing is known as to the cause of the fire except that it followed an explosion in the char house.

On April 11th, Henry Pemberton, former Vice-President of the Pennsylvania Salt Manufacturing Co., died in Philadelphia at the age of 85 years. Mr. Pemberton was well known as a manufacturer, scientist and author.

Dr. G. D. Rosengarten has been elected by the Executive Committee of the Division as Chairman of the Industrial Division of the American Chemical Society in place of Dr. George C. Stone, resigned.

The Mitchell Varnish Works have moved their plant from Newark, N. J., to Camden, N. J., where they also have their offices.

The Casein Co. of America is erecting a plant in Hagerstown, Md., for the manufacture of dry milk powder.

CONSULAR AND TRADE NOTES.

NITRATE INDUSTRY OF CHILE.

Minister Henry P. Fletcher, Santiago, submits the following data relative to the nitrate industry of Chile, based upon a report recently issued by the Nitrate Propaganda Association:

The production of nitrate in Chile for the years 1908, 1909, 1910, and 1911 (estimated), and the increased production in each year over the one preceding, were as follows, in quintals of 101.6 pounds each:

Years.	Produc- tion. Quintals.	Increase over preced- ing year. Quintals.	Years.	Produc- tion. Quintals	Increase over preced- ing year Quintals
1908	41,751,284	1910	52,500,000	7,705,535
1909	44,794,465	3,043,181	1911 (estimated)	55,000,000	2,500,000

These figures are slightly higher than those given in official statistics. In 1910 there were shipped to the United States over 12,000,000 quintals, as against 8,000,000 in 1909.

The increase in exportation over the preceding year was 1,804,989 quintals in 1909 and 4,369,196 quintals in 1910; the increase in consumption was 4,559,769 quintals in 1909 and 6,814,052 quintals in 1910.

The figures relative to the stocks of nitrate on the coast December 31, 1910, prepared by a special commission, show a total of 9,916,278 quintals.

A Reuter dispatch from Santiago de Chile estimates the production of nitrates for 1911 at 55,000,000 quintals and the world consumption at 53,860,000 quintals, and states that nine establishments are nearing completion which will produce 11,000,000 quintals a year.

DUST-PROOF CEMENT BAGS FOR AUSTRALIA.

Consul General John P. Bray, Sydney, reports that differences have arisen between the local cement manufacturers and the Wharf labors at Sydney, over handling cement in bags, the dust from which the laborers claim injures their health. The wharf laborers have virtually refused to handle bagged cement, which seriously hampers the trade.

The output of the leading cement factory is about 36,000

bags per week, of which 8,000 to 10,000 bags are shipped to other Australian States. Recognizing that immediate steps must be taken to save this interstate market, the company has made a trial shipment of cement in bags lined with paper. It is stated that the present cost of these paper-lined bags makes their use almost prohibitive, but that, if the experiment proves successful, arrangements will be made to make such bags by machinery.

As this matter may interest manufacturers in the United States, some of whom produce bags of paper stock strong enough to convey coal, it is suggested that they correspond with the company in question (address may be secured from the Bureau of Manufactures).

LITHOPONE IN GERMANY.

Consul General Robert P. Skinner reports that lithopone is manufactured in some 12 factories, of which three are in Silesia, two in the Duchy of Brunswick, one in Thuringia, two in Nassau, three on the lower Rhine, and one in Bavaria. The capacity of these factories per annum varies between 1000 carloads at the most important and 100 at the smallest.

In addition to its various uses in the paint trade, lithopone is also being employed in the manufacture of many rubber articles, linoleum, oilcloth, sealing wax, and artificial stone. The consumption of lithopone will increase steadily, although there is no doubt an overproduction at this time.

GERMAN INCANDESCENT-LAMP INDUSTRY.

Official statistics of the production of incandescent lamps, now being compiled in connection with the new Government tax upon lighting apparatus, have so far been made public only for the six months from October 1, 1909, to March 31, 1910. The following table gives the total number of the various kinds of incandescent lamps manufactured and imported.

Kind of lamp	Produced	Exported	Imported
Filament:			
Carbon	13,994,323	8,397,756	566,115
Metal	17,828,730	12,303,719	141,407
Nernst burners, etc.	253,456	141,965	448
Burners for mercury-vapor lamps.	4,541	1,617	79

MINERAL PRODUCTION OF BRITISH COLUMBIA.

The total mineral production of British Columbia for 1910, compared with 1909, as shown in Government reports, was as follows:

Articles.	1909.	1910.
Gold:		
Placer.....	\$477,000	\$482,000
Lode.....	4,924,090	5,198,505
Silver.....	1,239,270	1,282,500
Lead.....	1,709,259	1,480,000
Copper.....	5,918,522	4,972,500
Zinc.....	400,000	184,000
Total.....	14,668,141	13,599,505
Coal.....	7,022,666	9,800,000
Coke.....	1,552,218	1,284,000
Building materials, etc.....	1,200,000	1,500,000
Grand total.....	24,443,025	26,183,505

DECLINE OF INDIAN INDIGO.

Consul General Wm. H. Michael, Calcutta, reports that during 1896 India's indigo industry had reached its greatest prosperity. Exports of 20,981,744 pounds were valued at \$17,848,370.

By adhering to old methods of cultivation the Indian planter has permitted the more progressive synthetic dye manufacturer to surpass him, and in 1906 Indian indigo exports had fallen to 3,920,000 pounds, valued at \$2,333,333. Since then the decline has been continuous. During the fiscal year ended March 31, 1910, it had fallen to 2,022,832 pounds, with a valuation of only \$1,172,718, and this year it will, no doubt, be still lower.

LARGE GRAIN CROPS IN ROUMANIA.

The Roumanian consular officer in London states that the total value of grain production in his country for 1910 was \$253,000,000 or \$20,000,000 greater than for 1906, when crops were very abundant. The wheat crop alone was worth about \$100,000,000 and the corn crop about \$60,000,000. He adds that Roumania will have to provide the largest share of corn for European requirements this year.

BOOK REVIEWS.

Nitrocellulose Industry. By EDWARD C. WORDEN. Vol. I [Vol. II in press], 565 pp., 148 illustrations. D. Van Nostrand Company, New York, 1911. Price, \$5.00

The first volume of this work comprises the following subject matter: Cellulose, its sources, properties and modifications; Cellulose Nitrates, their history, properties and analysis; Manufacture of Nitrocellulose; Solvents treating especially of fusel oil, amyl acetate and camphor; Paint Removers and Turpentine Substitutes; Pyroxylin Solutions and Lacquers including their preparation, properties and uses; Imitation Leather; Pyroxylin Coated Enamel and Patent Leather; Artificial Filaments describing the Chardonnet, Cuprammonium and similar processes together with the spinning, properties and uses of artificial silk.

Obviously it would be impossible for one person to be personally familiar with all the processes outlined above, and in treating the subject the author has drawn freely from the journal and patent literature. In the chapter on Solvents and Non-Solvents and that on Pyroxylin Coated Enamel and Patent Leathers, however, he writes from his own experience and especially in the first mentioned chapter, contributes much that is valuable.

In this chapter, which is typical, a careful account is given of the first work done on solvents and their development up to the present time. This account is accompanied by notes in smaller type, often covering over half the page, in which an unusually complete bibliography is given with short reviews of the subject matter of the references in most cases. Also elaborations are given in the notes of the text above, enabling the reader to get more specific information where desired.

To consider the chapter on solvents more in detail, a very clear idea of the uses and functions of the various solvents of pyroxylin is given under the heading "Classes of Solvents." Under the heading "Acetone,"

a lucid explanation is given of the parts played by the different ingredients of a pyroxylin solution. Here, as in the rest of the work, the commercial side of the question is kept steadily in view and the cost of a solvent is considered along with its other properties; thus the use of benzene in lowering the cost of solutions is well set forth in the statement of "Stevens' Law."

The sub-headings of the above chapter, as in the case of many of the other chapters, are not logical or well chosen. For example, the first few paragraphs differ from most of the other paragraphs in the book in having no heading at all and gradually change from a historical account of solvents to a discussion of their relations to each other in their action on nitrocellulose. Thus some valuable data would be lost by a reader making use of the headings in heavy type. Where the headings are given, they are often misleading as, to give a further example, phenyl acetate follows the paragraph of non-solvents along with the headings "Chloroform," "Carbon tetrachloride," etc.

This same haphazard arrangement is also noticeable in the matter contained in the different chapters, a paragraph on methyl alcohol being included in the chapter on fusel oil which, may it be said parenthetically, makes itself prominent by the extraordinary statement that acetone-free methyl alcohol is a non-solvent of industrial cellulose nitrates.

Besides putting subjects out of their logical place much matter is included which is irrelevant in a book on the nitrocellulose industry; for example, there is a whole chapter on paint removers, a sketch of the tanning industry in Chapter XII and an account of cuprammonium and other non-nitrocellulose filaments in Chapter XIII. Thus a wonderfully complete but not very well digested pile of facts is brought together, which, although they may be located by

means of the excellent index, make the book cumbersome and tedious to read in many places.

Included in this vast amount of information are many excellent descriptions of technical processes, accompanied by illustrations of apparatus. These include numerous nitrating processes, methods and contrivances for making pyroxylin solutions, the refining of fusel oil and manufacture of amyl acetate, leather-coating compounds and machinery for applying them, and the manufacture of artificial filaments.

Not nearly as valuable are the analytical methods given for the determination of nitrogen, the analysis of mixed acid and the assay of amyl acetate, also Redpath's method of acid calculation, all of which need editing by one who has made use of them in factory practice. It would be better to give an outline of the methods than to give actual procedure which is incomplete and misleading.

Viewed in perspective, the various faults here mentioned do not detract seriously from what is undoubtedly the most valuable and complete work on the subject of nitrocellulose yet published. The student and general reader will find much of interest in the historical accounts and the descriptions of the manufacture of many familiar articles, while the technician will find the bibliography and résumés of patent and journal references invaluable. C. M. JOYCE.

Elementary Chemistry for Coal-mining Students. By L. T. O'SHEA, M.Sc. (Sheffield), B.Sc. (London). Professor of Applied Chemistry in the University of Sheffield. 12mo., 319 pp. Longmans, Green and Co. 1911. \$1.80 net.

This very readable volume has been the gradual outgrowth of many years of lectures, delivered before audiences composed largely of students of coal-mining, ignorant of chemistry, which may explain the semblance of crudity and lack of continuity occasionally to be found in the text. This crudity, or lack of precision in the formulation of laws and the statement of facts, is apparently intentional and should be no drawback, as the audience for whom the work is primarily intended would be largely incapable of appreciating fine distinctions, and would be but confused by them. The lack of continuity may be attributed to the lecture origin of the work. It would appear that many of the chapters have originally been lecture themes, and even though arranged in logical sequence, there is often but little connection between them.

While this book is termed a work on chemistry, it is really a compilation of data pertinent to the science of coal-mining, the pure chemistry being secondary to, and explanatory of, these data. The text is so worded, and the chapters so arranged, that the facts of most importance are kept largely free from chemical theory, so that their salient points may be readily grasped, without entering into the pure chemistry. This chemical theory is profusely illustrated by the description of well chosen experiments.

The mining profession at large owes a debt of gratitude to the author of this estimable work for

the many valuable facts and tables, which have been carefully gleaned from a great mass of literature. Perhaps some slight idea of the wealth of information stored in this volume may be gathered from a brief résumé of its more important chapters.

In the chapter on the atmosphere, besides the usual statements regarding its composition and constituents, the spontaneous ignition of coal is treated of at length. The theoretical consideration of the origin of this evil and its remedy are dealt with. Extinctive and irrespirable atmospheres are made the subject of another section of this chapter, in which very interesting tables are given, showing the percentage composition of atmospheres extinctive of the flames of various burning substances. The physiological action of atmospheres depleted in oxygen is also briefly treated.

A chapter is devoted to a very thorough and concise discussion of gas, and atmospheric pressures, with a description of the various types of barometer, and water gauge, used for the measurement of these pressures. It may be noted here that the mathematical considerations throughout the book are simple and uninvolved, and may be readily followed by the least initiated.

Following the usual chapter on water and its composition is found a chapter on pure chemistry, treating very simply of atoms and molecules.

The chapter on sulphur is remarkable for nothing save that a brief outline of the physiological action of hydrogen sulphide is given, and that the "iron disulphide" associated with coal is described as iron pyrites, no mention being made of the presence of marcasite.

Under carbon, tables are given showing the composition of various cokes and charcoals, as well as analyses of samples of fire-damp.

The chapter dealing with flame and the safety-lamp is full and well written. Cuts are given showing the appearance of different shaped flames burning different fuels in atmospheres containing varying quantities of methane. The conditions to be fulfilled by an efficient safety-lamp are clearly stated with a description of the more important types of this lamp and their advantages and drawbacks.

The subject of coal is treated fully and clearly. As might be expected, much stress is laid on the description of the coking of coal and the by-product oven, which is amplified by a special chapter discussing these by-products and their recovery.

The subject of explosives is especially well handled. The physical effect of high and low explosives, when detonated, and their dynamic testing is detailed. A section is devoted to the length of flame from explosives, while the requirements to be fulfilled by such bodies when used in coal mines are discussed, as well as the subject of "permitted explosives" with the tests to which these are subjected. The general consideration of safety in handling of explosives forms the topic of another section, while throughout the chapter many analyses of these substances are quoted.

In the chapter on explosion in gases, the description of several colliery disasters are abstracted. The whole subject is roughly divided into two types, that of a pure fire-damp explosion, and that of a fire-damp explosion continued and magnified by coal dust.

The mechanics of the propagation of flame through an explosive mixture of a combustible gas and air is lucidly explained. The various experiments carried on in England to ascertain the explosibility of coal dust are described.

The book is concluded by a chapter dealing with the physical consideration of the effects of pressure and temperature on gases, another on chemical calculations, and several appendices of useful tables.

EDWIN M. CHANCE.

Zur Kenntnis der Cellulosearten. VON DR. WALTER SCHULZ. Introduction by Dr. Carl G. Schwalbe. Verlag von Gebrüder Borntraeger, Berlin. 1911. 100 pp., 3 illustrations. 3 Mks., 20 Pf.

The identification of cellulose fibers is usually accomplished by the aid of the microscope and very seldom by strictly chemical means. Even in these cases the investigation is usually done by micro-chemical methods. The author in this book has collected the latest chemical methods for the determination of the various intermediate decomposition products of cellulose and the various constants used in testing sulphite cellulose.

The work of the author can be divided into two parts: Part I deals with the methods of production and characterization of the intermediate decomposition products of cellulose, such as the vegetable parchment, the Guignet cellulose, the amyloid of Flechsig, the acid cellulose of Ekström, etc. The end-products of the hydrolysis of cellulose have also been considered as to methods, yield, etc.

Part II describes the physical-chemical methods as tried out by the author for determining the various constants of sulphite cellulose.

The author has added in this little work a valuable addition to our knowledge of the little-known field of cellulose chemistry and cellulose testing.

O. KRESS.

Composition and Heat Treatment of Steel. By E. F. LAKE. x+252 pp., 143 illustrations, \$2.50. McGraw-Hill Book Company, New York. Second Edition, Revised and Corrected.

This book is not worthy of a review, yet it would be unfair to say that it is of no value. It is fair, however, to say that many of the sentences and paragraphs are loosely constructed and their meaning vague and obscure. Many of the statements are in error and truths stated correctly in one part of the volume are contradicted in another part.

To point out all the errors and put the seemingly intended thought of the author in plain simple language would make a volume larger than the book itself.

The following quotation will serve to illustrate the character of the book:

Page 1, paragraph 3: "In making steel, the opera-

tion begins by making pig iron from the iron ore, which is a natural iron rust or a combination of iron and oxygen. The oxygen is removed by combining iron ore, coke, and limestone in a furnace, as shown in Fig. 2, and heating to a high temperature by injecting superheated air into the bottom of the furnace. The coke is burned by the oxygen in the air; a part of it aids in maintaining this high temperature while the rest is useful in removing the oxygen."

Page 13, paragraph 4, discussing blown metal: "Except for the impurities which poison the metal, namely phosphorus, sulphur, oxygen and possibly nitrogen, it has become for all practical purposes a pure metal that is very brittle. This makes it necessary to add certain ingredients that will toughen, strengthen, and harden it so as to make it useful and workable."

Page 64, paragraph 5: "Carbon unites with chemically pure iron in all proportions up to 4½ per cent. The capacity of the iron for carbon can be increased by using manganese, and when a high percentage of manganese is added to steel the carbon content can be raised to 7 or 8 per cent."

Page 73, paragraphs 4 and 5: "Manganese is not only useful to cleanse the bath of impurities, but it has other properties that aid in making steel better. The amount that can be left in the steel varies with the amount of various other ingredients that are added to the metal, and this is especially so of carbon. In effect it behaves in practically the same manner as carbon, as also does nickel. With a given carbon content the introduction and increase of manganese causes a series of structural changes similar to those that occur in carbon steels, that only contain small percentages of manganese.

"While the action of these three elements upon iron is of the same kind, it is not of the same strength, as the equivalent of 1% of total carbon, that contains the maximum amount of hardening carbon, is 7.25 per cent. of manganese and 17.55 per cent. of nickel. All three of these cause a structural change in the metal from pearlite, that includes the sorbitic, to martensite, that includes the troostitic, and then to the polyhedral structure, and with none of them is a special carbide formed. Chromium has an analogous effect, but not as complete, as a double carbide of iron and chromium forms and this is not maintained in solution in the iron without tempering."

Page 75, part of paragraph 3: "Many contradictory statements have been made as to the effect of silicon on steel. When the silicon is high in Bessemer steel it is an indication that the metal has been blown too hot, and the metal is apt to be brittle. The percentage varies considerably, according to the heat of the charge, and this causes irregularities which may account for the difference of opinion. The melting point and specific weight of pig iron are governed chiefly by the silicon and the carbon, which are the principal elements."

Page 78, paragraph 3: "In the rolling mills phosphorus does not show any bad effect, as the heat under which the steel is worked seems to overcome this,

but when the metal has become cooled and is subjected to sudden shock or to vibrational stresses, it breaks very easily. The lower the temperature and the higher the atmosphere the easier will the breaks occur. This has led to the term 'cold-shortness' as applied to the effect of phosphorus on steel."

Page 121, paragraph 2: Direct Steel Castings. "In this process the metal is taken direct from the furnace to a heated mixer where the proper materials are added to make the required quality of steel. The metal can be kept liquid as long as desired in the mixer, and its chemical properties adjusted by the addition of different materials. The mixer is kept full by transferring metal from the furnace. When the metal is wanted for casting the mixer is tapped and the metal run into ladles, from which it is poured into the molds as in other castings."

Page 193, paragraph 7: "Cementite is the carbide

of iron, and is expressed by the following formula: Fe_3C , which means ferrite—which is pure iron—3 atoms for every one atom of carbon. It is the second constituent in importance in steel—ferrite being first—and is very hard and brittle. Practically all the carbon is present in this form, and it usually crystallizes in thin flat plates. Cementite does not exist in pure iron, which contains no carbon, and of itself contains about 6.6 per cent. of carbon, which is about one-fifteenth of it."

I have never before read in any book such a conglomerated mass of facts and misinformation.

The binding and paper of this book are good; the print clear and well defined; the illustrations are excellent.

It is to be regretted that the publishers should have permitted such a book to go out without the exercise of greater editorial skill.

WILLIAM BRADY.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

METAL AND ORE PRODUCTION.

In an advance chapter of "Mineral Resources of the United States," by Waldemar Lindgren, of the United States Geological Survey, covering the metal production of the United States for 1909, the Survey has adopted the common-sense plan of reducing all values to a single unit of measure, namely, the short ton of 2,000 pounds. The comparative figures for 1908 and 1909 are issued in this form, covering the production of the different metals, and also the crude metalliferous ores. They show at a glance the quantities of metals and ores produced and their relative quantitative importance.

Mr. Lindgren also includes, in this statement, the large quantities of imported ores, unrefined bullion, etc., which are refined in this country, thus adding to the figures of production from domestic ores as stated in the usual tables. In 1909, for instance, the total production of domestic ores of gold, as stated in the gold chapter of "Mineral Resources," was \$99,673,400. The total production, however, including gold refined from foreign ores, matte, etc., was \$126,099,632.

Comparison of the 1908 and 1909 figures thus stated shows in most items a marked increase. Pig iron increased from 17,678,080 tons, valued at \$248,733,369, in 1908 to 28,638,883 tons, valued at \$411,544,773, in 1909. Of copper 568,981 tons, valued at \$150,210,984, were produced in 1908, as against 695,510 tons, valued at \$180,832,600, in 1909. The platinum production in 1908 was 0.026 ton, valued at \$14,250, which increased in 1909 to 0.039 ton, valued at \$28,440.

The chapter also states the production of crude ores from domestic ores, a showing which has not been attempted in any prior year, and also gives figures on the concentrates of several metals. It is interesting to note that while the production of crude zinc and zinc-lead ores in the United States in 1909 was 10,679,608 tons, the production stated in zinc concentrates was only 715,300 tons.

The crude ore mined in 1908 was 85,627,624 tons and in 1909 it was 112,056,302 tons. An estimate is made of the volume of gold-bearing placer gravel washed in 1909, which is stated to be 80,000,000 cubic yards in the United States, with an average value of 12 cents a cubic yard, and 4,418,000 cubic yards in Alaska, with an average value of \$3.66 a cubic yard.

CLAY PRODUCTS IN FAVOR.

The year 1909 was a record breaker for clay products—bricks, tile, pottery, etc.—The value of the output being \$166,321,213, as compared with \$133,197,762 in 1908. The value was higher than that of 1907 (\$158,942,369). The United States Geological Survey has just issued an advance chapter of "Mineral Resources of the United States" for 1909—"Clay-Working Industries," by Jefferson Middleton—which shows the year to have been a remarkably prosperous one in this important industry. In brick and tile products every item except fancy brick, sewer pipe, and stove lining increased in value. In the pottery industry every item showed an increase. The imports of pottery showed a gain of less than 1 per cent., although the domestic product gained 23.53 per cent. and the exports of high-grade domestic pottery likewise increased. The exports of all clay products increased 22.24 per cent. Every State and Territory except Alaska, but including Porto Rico, is a producer of burned clay, and 42 States showed gains.

The following are the 10 States with highest recorded production for 1909:

State.	Brick and tile.	Pottery.
Ohio.....	\$16,929,885	\$13,416,356
Pennsylvania.....	19,403,944	1,782,769
New Jersey.....	9,380,958	7,791,136
Illinois.....	13,505,898	838,555
New York.....	10,270,227	1,887,209
Indiana.....	6,744,295	900,928
Missouri.....	7,367,061	73,122
Iowa.....	4,846,706	51,990
California.....	4,312,590	124,575
West Virginia.....	1,159,627	2,350,470

The great growth shown in some of the clay-working industries during the last decade is interesting. Common brick increased from \$38,621,514 in 1900 to \$57,251,115 in 1909; vitrified paving brick from \$4,764,124 to \$11,269,586; front brick from \$3,864,670 to \$9,712,219; drain tile from \$2,976,281 to \$9,799,158; sewer pipe from \$5,842,562 to \$10,322,324; and fireproofing from \$1,820,214 to \$4,466,708.

NATURAL GAS PRODUCTION FOR 1909.

The chapter on natural gas from "Mineral Resources of the United States for 1909" can now be had of the United States

Geological Survey by application to the Director at Washington. The industry surpassed in 1909, both in the quantity and value of the gas produced, the record of any previous year, the estimated value being \$63,206,941, as against \$54,640,374 in 1908. Although the returns are unusually late, it is believed that as a result of coöperation with the Census Bureau they are more complete than those of any previous year. The report discusses the production in considerable detail and gives the output by States covering a long period of years. In 1909 Pennsylvania led with an output valued at \$20,475,207, West Virginia came next with \$17,538,565, Ohio was third with \$9,966,938 and Kansas was fourth with \$8,293,846. No other State produced as much as \$2,000,000 worth.

INCREASE IN GOLD AND SILVER PRODUCTION.

A report on the production of gold and silver in the United States in 1909, by H. D. McCaskey, of the United States Geological Survey, has just been issued as an advance chapter of the Survey's volume "Mineral Resources." The figures agree with those of the Director of the Mint, being the result of co-operation between the two bureaus, and are therefore final for both. The gold production was valued at \$99,673,400 and the silver at \$28,455,200, an increase over the figures for 1908 of \$5,113,400 for gold and \$404,600 for silver. The report includes figures and detailed statements of production by States, and comparisons of the total output for the last three decades. It also includes the statistics of imports and exports as well as tables of ore production.

SEVEN MILLION DOLLARS FOR MINERAL WATERS.

The sales of mineral water in the United States during 1909, according to the United States Geological Survey, represented a value of \$6,894,134, a slight increase over the figures for 1908. The quantity sold was 64,674,486 gallons and the average retail price was 11 cents a gallon. In addition to this quantity over 6,000,000 gallons were estimated to have been used in the manufacture of soft drinks. The tables given in the report show a steady increase in the production of mineral waters for the last 25 years, the figures for 1885 being 1,312,845 gallons. The value of the imports of mineral water in 1909 was \$1,085,177, with an average of 31 cents a gallon.

The report shows the production by States with names of springs and other details.

QUALITY OF ILLINOIS RIVER WATERS.

The United States Geological Survey has just published another edition of its exhaustive report on the quality of the waters of Illinois (Water Supply Paper 239). While this report is of first interest to the people of Illinois, it contains much information on steam pollution, the treatment of impure waters for municipal engineering and other industrial uses, the cost of differing degrees of purification for different purposes, and similar subjects having a general application and interest. The volume is now available for distribution and can be obtained on request to the Director, United States Geological Survey, Washington, D. C.

NATURAL GAS IN TRINIDAD.

The island of Trinidad, according to the United States Geological Survey, is well supplied with natural gas, large supplies of which are reported to be going to waste. This gas, if piped to Port of Spain, would undoubtedly be a great source of revenue. The gas is under great pressure, the discharge from a well at Guayaguayana being said to be about 1,000,000 cubic

feet a day. Every oil well drilled on the island thus far has produced large quantities of gas in addition to the oil.

Examination of the Raw Materials, Products and By-products of the Sugar Industry. By R. FRUEHLING. Brunswick. 8vo., 535 pp. \$3.75.

The Analysis of Paints and Painting Materials. By GARDNER and SCHAEFFER. 1911. L. 8vo., 109 pp. \$1.50. D. Van Nostrand Co.

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An Improvement in the Method of Malt Analysis. JAMESO'SULLIVAN. *Journal of the Institute of Brewing*, Vol. XVIII, No. 1, pp. 35-48. 1911.**Manufacture of Aerated Waters.** WALTER A. RILEY. *Journal of the Institute of Brewing*, Vol. XVII, No. 2, pp. 117-145.

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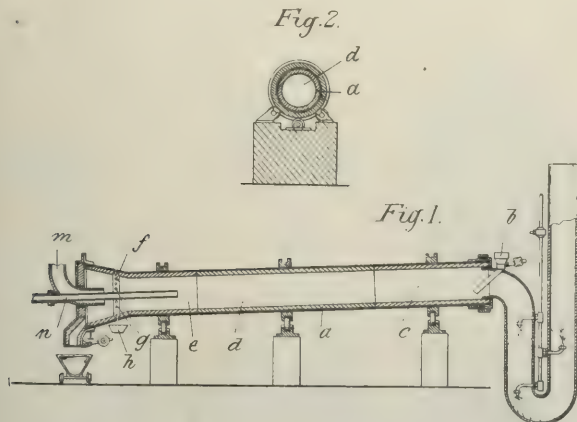
RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

986,271. Process of Refining and Agglomerating Ores and the Like.

This invention relates primarily to the treatment of those ores which can be smelted only with difficulty, first on account of their physical condition and secondly on account of the injurious foreign substances which they contain. To this class belong more particularly the friable iron ores.

According to this invention the revolving furnace, shown in the accompanying illustration, is heated by a water gas flame whereby new results are achieved. By the employment of a water gas flame, not only can all the results heretofore obtained be effected in a simple and certain manner, but it is also possible (owing to the peculiar formation of the flame) to so perform the operations in the furnace that oxidation or reduction and fusion shall take place at will.



In the patentee's apparatus shown in the accompanying illustration, *a* is the revolving drum which is lined with an acid or basic refractory material, and into which the ore is charged as its upper end through the chute *b*. The ore first passes through the drying zone *c* and then enters the oxidizing zone *d*. Here, the sulphur, arsenic, zinc and the like are oxidized and also volatilized, while the residual ore begins to fuse together in lumps and nodules. Any zinc which has not yet been volatilized as zinc oxide passes into the reducing zone *e* where it is volatilized as metallic zinc. Any lead that may be present is also reduced and melted here, and runs off through the annular passage *f* (which is provided with apertures *g*) into molds *h*. The ore passes out from the lower end of the furnace not only in a physical condition adapted for blast-furnace treatment, but also purified, and in a lower stage of oxidation.

For the purpose of keeping the oxidizing and reducing zones effectually separated from each other, the gas and air are pref-

erably admitted wholly or partially at different places. The wide pipe *m* serves for the admission of the water gas which can become ignited at the mouth of this pipe even without any previous admixture of air, while the quantity of air which is necessary for complete combustion or the excess air requisite for oxidation is admitted through the air pipe *n* at a place situated farther back.

By regulating the quantities of gas and air admitted, as well as by the manner in which and the place whereat the gas and air are mixed together, every possible desirable result can be obtained. This adaptability of the furnace constitutes its chief value, since it enables materials to be treated which have no homogeneous or uniform composition.

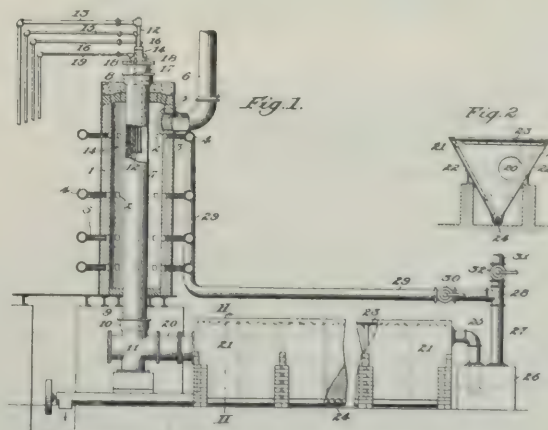
The furnace is to be used in the same manner whether iron ores, copper ores or by-products containing a high percentage of copper are to be treated, the lead, zinc, sulphur, arsenic and antimony being similarly separated. These separated products may be recovered for use according to the special economic conditions in each case. As will be seen by reference to the illustration that the waste gases may be cooled by means of a water spray so the volatile metallic oxides are precipitated in the form of mud and may be removed in that condition.

The inventor is Hugo Dicke, of Frankfort-on-the-Main, Germany, assignor to Jacob Eduard Goldsmid, of Frankfort-on-the-Main, Germany.

986,489. Process of Dissociating Acetylene.

This invention is a process of dissociating acetylene by heat, at approximately atmospheric pressure.

The patentee of this process found that acetylene at practically atmospheric pressures, if suddenly heated to a temperature at or in excess of that corresponding to a dull red heat, dissociates



instantly and quietly into its elements of carbon and hydrogen without the production of any of its polymers, and that the carbon so produced is either deposited in the heating retort, or is carried along with the gaseous hydrogen as a light flocculent powder, easily handled and practically chemically pure. His process of making lampblack from acetylene is based on this discovery.

In using the apparatus illustrated to carry out the process, the retort 7 is heated, preferably by gas introduced through the burners 3, to or above the temperature of dull redness.

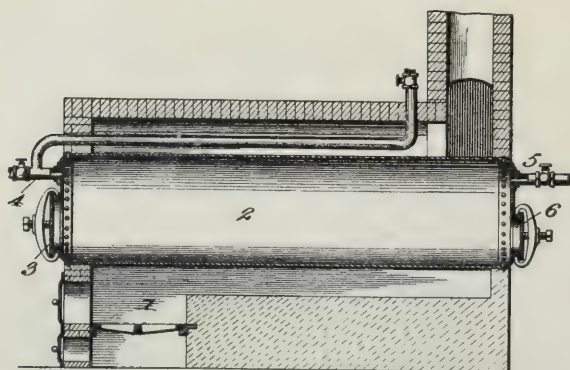
A stream of acetylene, maintained at a temperature below its dissociation point by the water flowing through the jacket 14, is then delivered through pipe 12 into the upper end of the retort. The acetylene, issuing into the retort and suddenly heated to or above the temperature of dull redness, instantly and quietly dissociates, the carbon being set free in the form of lampblack, which largely collects in the retort, while the free hydrogen passes on through the settling chamber 21 and may be returned to the burners 3 to heat the retort. The current of hydrogen may also carry some of the lampblack into the settling chamber. As the retort becomes filled with lampblack, the stream of acetylene is cut off, valve 30 in hydrogen pipe 29 is closed and valve 32 in waste-pipe 31 is opened. An inert gas, preferably at the temperature of the retort, for example hot products of combustion, is then forced into the upper end of the retort through the nozzles 18, blowing the light lampblack out of the retort and into the chamber 21, where it settles, to be removed by the conveyor 24.

The inventor is John M. Morehead, of Chicago, Illinois, assignor to Union Carbide Company, of Chicago.

987,674. Process of Producing Nitrogen Compounds.

This invention relates to a process of producing nitrogen compounds from carbids.

In the production of nitrogen compounds by the reaction of nitrogen with carbids, as for example, the carbids of the alkaline earths, it has been ascertained that it is not necessary for the process that the entire mass of the carbid be brought to the temperature necessary for the reaction by supplying external or intrinsic heat to the entire mass; but that it suffices if this temperature be produced at one place in the mass, when the reaction then continues spontaneously throughout the entire mass. A preliminary condition, however, is that the reaction temperature of from about 800° C. to 1100° C. be actually attained at this one place.



In accordance with the present invention the process may be carried out in several ways, of which the following are examples:

The ignition at one place may be produced by a convenient heating means involving heat by chemical reaction, which will raise the temperature at that place to the temperature required for the conversion of the carbids, whereupon the conversion will proceed spontaneously throughout the mass, sufficient nitrogen

being present to effect the conversion. The production of a temperature sufficiently high for the absorption of nitrogen by the carbid at one place or point of the carbid by means of said chemical heating in order to raise the carbid at this one place to the proper ignition temperature may be accomplished: (a) by means of a primer comprising an explosive mass or the like; or (b) by means of substances reacting with carbid with the production of the necessary heat, which substances, if in the solid state such as chlorate of potassium, nitrate of alkali, etc., may be added to the carbid at the place of ignition; while if the substances are gaseous, such as chlorine or oxygen, the same may be added to or employed with the first portions of the nitrogen that are led to the carbid until the ignition has taken place; or (c) the requisite temperature may be produced by substances such as magnesium or aluminium which, when mixed with the carbid at the place of ignition, react with the nitrogen with the production of the desired heat. After the ignition has produced a temperature sufficient to cause a further absorption of the nitrogen, the latter is further supplied, and it will continue to be absorbed with a further development of heat so that the continued supply of nitrogen will cause the absorption to proceed spontaneously throughout the mass.

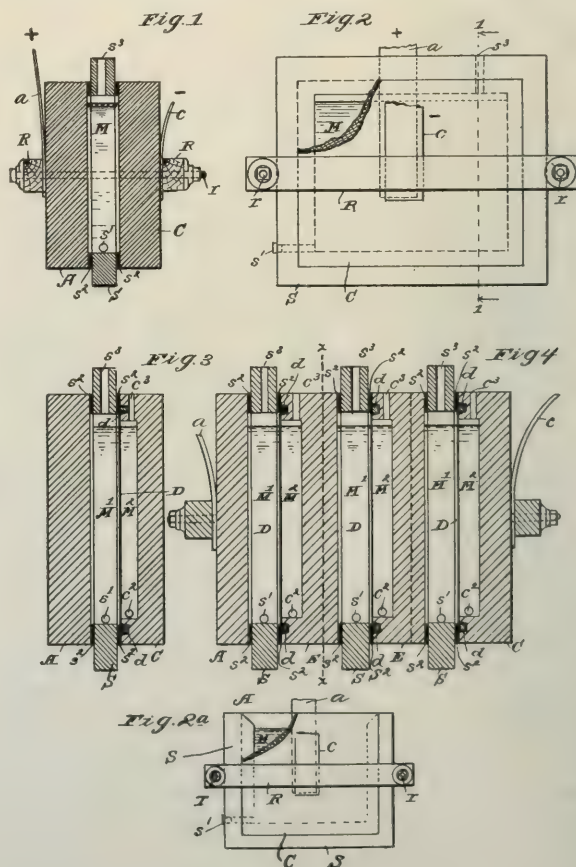
The accompanying illustration shows apparatus in which the process may be practiced.

The inventor is Albert Randolph Frank, of Halensee, near Berlin, Germany; assignor to the Firm of Societa Generale Per la Cianamide, of Rome, Italy.

987,717. Electrolytic Cell.

This invention relates particularly to electrolytic cells for the electrolysis of alkaline chlorides.

By reference to the accompanying illustration, the cell will be seen to comprise a rectangular ring-shaped, or perforated, member, S, which is termed a separator. Upon the opposite



sides of such separator, which is made of suitable insulating material, are clamped blocks or plates, A C, of carbon. These plates, A C, laterally enclose the opening through separator S, thereby forming a cell or chamber, M, for the reception of the electrolyte. Electric current leads, *a c*, are clamped in contact with plates A C respectively by the same clamps, R, which thus hold the latter against separator S, such clamps, R, consisting simply of wooden bars, the ends of which extend beyond the ends of the blocks in question and are joined together by threaded bolts, *r*. Where separator S is of the annular form shown, chamber M will be a closed chamber save for the opening *s*³ provided for the introduction of the electrolyte as occasion may arise as well as for escape of gas from the cell and an opening, *s*⁴, normally closed, for draining the cell of its contents. If, however, an open cell is desired this result is accomplished by making the separator of U-form instead of a complete annulus or ring. In the use of the cell the chamber M will be charged with the electrolyte, as, for example, a solution of common salt, and an electric current passed through it from A to C. Such plate, A, thus becomes the anode, upon the active face of which chlorine will be liberated while plate C acts as the cathode upon the active face of which hydrogen and caustic soda are liberated.

The inventor is Thomas Griswold, Jr., of Midland, Michigan.

982,673. Insoluble Nongelatinizable Starch.

This invention relates to a method of treating starch or starch-containing materials for the purpose of converting it into a hitherto unknown form, which owing to several characteristic properties thereby acquired renders the starch more useful and more valuable for certain purposes as, for instance, in nitrating starch, in manufacturing glucose from starch, etc.

The most characteristic property of starch is its ability of paste-forming or gelatinizing when heated with water above a certain temperature, which varies somewhat for the different kinds of starch. The treatment to which the patentee subjects the starch has for its object to deprive the starch of its ability of gelatinizing when heated with water.

In the practice of the process the starch or starch-containing material is steeped in a solution containing from about five to ten per cent. of formaldehyde and a quantity of an ammonium salt whose content of ammonium is theoretically sufficient to form with the formaldehyde hexamethylenetetramine, although an excess of either reagent, if not too large, will not materially alter the results. The patentee has used in his experiments mostly ammonium chlorid, but has obtained as good results with other ammonium salts, especially inorganic, as for instance ammonium sulphate provided sufficient material was used and the time of reaction was modified. Starches from different sources vary to some extent in their behavior to such a mixture of formaldehyde and ammonium salts, some requiring stronger solutions than others or a longer or shorter time of reaction. The main object of the invention being the production of an

ungelatinizable starch, the quality of starch and the particular ratio of the ingredients is left to the selection of the manufacturer.

The patentee prefers to use an aqueous solution containing from about 5 to 10 per cent. of formaldehyde and from 6 to 11 per cent. of ammonium chlorid to which the starch or starch-containing material is added until a perfectly thin milk is obtained. He preferably uses a ratio, one part of starch to about three or four parts of the solution, but any other convenient ratio may be used without interfering with the results. The whole of the mixture is kept at ordinary temperature, *i. e.*, 20° to 30° C., the ingredients being in intimate contact, until a small sample withdrawn from the mass and diluted considerably with water does not show gelatinization on heating, and the starch granules sink to the bottom of the test tube.

When the reaction is completed, the mixture is allowed to settle, the liquid drawn off and the residual starch filtered and washed, until the filtrate does not give any further reaction for the chlorine ion. It can then be dried. The starch thus obtained does not outwardly differ from ordinary starch, but is nevertheless changed into what may properly be called an allotropic form of starch with the properties described above.

The inventor is Bernard Herstein, of Bayonne, N. J.

Improved Process for Coating or Printing with Viscose.

British Patent 15306/09.

Dr. Leon Lilienfeld, Vienna.

Claims (1) a process for coating or printing with viscose either alone with coloring matters or pigments of all kinds, characterized by the fact that the known compounds of viscose with the metals of the magnesium group (zinc compound for example) are dissolved with the assistance of as much alkali as is necessary for replacing the metal of the magnesium group contained in the viscose compound by the metal of the alkali group; (2) method of carrying into practice the process in accordance with Claim 1, characterized by the fact that soaps soluble in water or sulphuric acid or other sulpho fatty acids of their sodium or ammonium salts are added to the printing or coating layers obtained in accordance with Claim 1 in quantities which are not smaller than one-fifth of the proportion of cellulose calculated in air-dry cellulose.

Improvements in the Production of Isoprene.

British Patent 27908/09.

H. Woltereck, London.

Claims the process of producing isoprene from turpentine, the operation of passing the vapors of the same in most intimate contact over heated iron either without or with the admixture of inert gases, such as nitrogen, and at a carefully regulated temperature between 5500 C. and 6000 C. substantially as described.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF MAY.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Acetanilid.....Lb.	20 1/2 @	23
Acetone (drums).....Lb.	13 @	15
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	2.33 1/4 @	2.45
Acetic Acid (28 per cent.).....C.	1.62 1/2 @	1.75
Acetate of Lime (gray).....C.	1.75 @	1.80
Acetate of Lead (brown, broken).....Lb.	7 3/4 @	8
Aniline Oil.....Lb.	11 1/2 @	11 3/4
Benzoic Acid.....Oz.	11 1/4 @	12
Boric Acid, crystals.....Lb.	7 @	7 1/2
Carbon Tetrachloride (in drums).....Lb.	8 1/8 @	12
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (in drums).....Lb.	10 @	11
Citric Acid (domestic).....Lb.	38 1/2 @	39
Camphor (refined in bulk).....Lb.	— @	49 1/2
Dextrine (imported potato).....Lb.	5 1/2 @	7
Dextrine (domestic corn).....C.	2.37 @	2.50 1/2
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....Lb.	21 3/4 @	22 1/4
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7.17 1/2 @	7.68 3/4
Pyrogallie Acid (bulk).....Lb.	1.00 @	1.05
Paraffine (crude) 120 @ 122 m. p.....Lb.	3 @	3 1/4
Paraffine (refined), domestic 120 @ 122 m. p.....Lb.	4 1/2 @	4 3/4
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	1.57 @	1.73
Starch (potato).....Lb.	4 1/4 @	5 1/4
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 7/8 @	5 1/4
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	29 1/4 @	29 1/2

Inorganic Chemicals.

Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (in drums) 16°.....Lb.	2 3/4 @	3
Ammonium Chloride, gray.....Lb.	5 3/4 @	6
Arsenic, white.....Lb.	1.82 1/2 @	2.06 1/4
Ammonium Carbonate, domestic.....Lb.	8 @	8 3/4
Aluminum Sulphate.....Lb.	90 @	1 3/4
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 1/4
Barium Nitrate.....Lb.	5 1/2 @	6 1/2
Borax, crystals in bags.....Lb.	3 1/2 @	4
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.19 3/8 @	1.28 3/4
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 1/4 @	4 1/2
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	90 @	92
Chalk (light precipitated).....Lb.	4 1/2 @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (in bags).....C.	62 1/2 @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 @	8 1/2
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	81 @	84
Nitric Acid, 36°.....Lb.	3 7/8 @	4 1/4
Nitric Acid, 42°.....Lb.	4 7/8 @	5 1/4

Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25
Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 3/4 @	11
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals, f. o. b. works.....Lb.	8 1/4 @	9 1/2
Potassium Nitrate (crude).....Lb.	4 3/4 @	5
Potassium Bichromate, 50°.....Lb.	7 3/8 @	7 3/4
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	66 @	70
Salt Cake (glass-makers).....C.	62 1/2 @	77 1/2
Silver Nitrate.....Oz.	34 1/2 @	37
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 1/4 @	5
Sodium Chlorate.....Lb.	8 1/4 @	9 1/2
Sodium Bicarbonate (English).....Lb.	2 3/4 @	3
Sodium Bichromate.....Lb.	5 5/8 @	5 3/4
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 1/2
Sodium Hydroxide, 60 per cent., f. o. b. works.....C.	1.80 @	1.85
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.	67 3/8 @	7
Sodium Nitrate, 95 per cent., spot...C.	2.10 @	2.12
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 3/4 @	10
Strontium Nitrate.....Lb.	7 3/8 @	7 3/4
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	90 @	1.00
Talc (American).....Ton	15.00 @	25.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	12 1/2 @	12 7/8
Tin Oxide.....Lb.	45 @	47
Tin Chloride (36°).....Lb.	11 @	11 1/2
Zinc Chloride (granulated).....Lb.	4 1/2 @	4 3/4
Zinc Sulphate.....Lb.	2 1/4 @	2 1/2
Zinc Dust.....Lb.	6 5/8 @	7

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 1/2
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	9 @	20
Corn Oil.....C.	6.10 @	6.15
Cottonseed Oil (crude), f. o. b. mill...Gal.	40 @	40 7/8
Cylinder Oil (light, filtered).....Gal.	19 1/2 @	20
Japan Wax.....Lb.	9 1/4 @	9 1/4
Lard Oil (prime winter).....Gal.	85 @	91
Linseed Oil (raw, city).....Gal.	91 @	92
Linseed Oil (double-boiled).....Gal.	93 @	95
Paraffine Oil (high viscosity).....Gal.	23 1/2 @	24
Rosin Oil (first run).....Gal.	— @	41 1/4
Spindle Oil, No. 1.....Gal.	14 @	14 1/2
Stearic Acid (double-pressed).....Lb.	9 1/2 @	9 7/8
Sperm Oil (bleached winter) 38°.....Gal.	82 @	85
Tallow (acidless).....Gal.	64 @	68
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum [No. 1 ingots].....Lb.	20 1/2 @	21
Antimony.....Lb.	9 1/2 @	9 5/8
Bismuth.....Lb.	1.80 @	1.90
Copper (electrolytic).....Lb.	— @	12 1/6
Copper (lake).....Lb.	12 1/8 @	12 1/3
Lead.....Lb.	4.37 1/2 @	4.40
Mercury.....Lb.	61.3 @	61.5
Nickel.....Lb.	40 @	50
Platinum (refined).....Oz.	42 @	42.50
Silver.....Oz.	— @	53 1/8
Tin.....Lb.	37 3/4 @	43 3/4
Zinc.....Lb.	5.4 @	5.45 2/3

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EDITORIALS

RETROSPECTION.

We may not need special evidence to convince ourselves that we are living in a rapidly improving technical age. The development of our industries testifies clearly on this point. That chemistry has an important part in this development, particularly in our own country, could be guessed from a knowledge of the fact that there are fully ten times as many chemists here as there were twenty years ago. These men are at work on more than ten times as many different materials as were known twenty years ago, and the end is not yet.

An interesting and instructive view of the rate of advance of chemistry in our era may be gained from a study of the known metallic elements.

It is plain that new chemical compounds, in general, are coming into commercial use so rapidly that it is hopeless to even attempt collection of data. It is safe to say that if we include organic compounds, there are many hundreds of new substances made and described each year. Hundreds of these will be useful for years, solely as systematizing marks for themselves and for other compounds, but in this way a very strong foundation is being built for the future of chemistry. Any adequate summary for this general field is impracticable because of its magnitude.

In case of the chemical elements a survey is more simple, and particularly with the metallic elements. The metallic elements have a special interest in this connection, because they are limited in number, their properties are known and some of them have been used for ages. A philosopher would probably maintain that as our wants become more and more differentiated, we will call into use more and more of this store of metals. This is practically what has been done in the past. That we still have no considerable use for metallic barium, for example, is explained by

an insufficiently developed requirement. More easily obtainable metals have thus far fulfilled needs which will finally grow so complex as to require metallic barium.

But this rate of increase in demand for new metals to fill new wants has not been a constant one—far from it. It never was nearly so rapid as at present, and it characterizes our technical age. We have in all about fifty elementary substances which we can call metals or metalloids. Not more than a very few others seem probable of discovery. We want to point out the rate of increase of use, to what we may call an appreciable extent, of these metals in their metallic state. This excludes from consideration uses of compounds or salts of the metals.

Of the fifty there were seven which were known and used commercially over two thousand years ago. These are iron, copper, tin, gold, silver, mercury, and lead. There are eight others which were introduced into practical use more or less extensively between the first and the nineteenth century. They are zinc, iridium, platinum, cobalt, nickel, antimony, cadmium, and bismuth, that is, the rate of addition has been less than one metal for each two centuries prior to our century. Within our own times, say about a quarter century, there have been about fourteen more metals added to commercial use, or a rate more than one hundred-fold greater than the previous rate.

These values may be modified somewhat by use of different criteria of commercial use, but the conclusions remain about the same.

We are now rapidly seeing practical use made of a large part of our little group of known metals. Those which have been introduced into commercial use during the past quarter century, either pure or intentionally alloyed, are aluminum, magnesium, silicon, cerium, vanadium, tungsten, tantalum, osmium, chromium,

selenium, molybdenum, titanium, boron and manganese. The rate of addition must soon rapidly fall off, but among those which seem to call for some attention and demand introduction is calcium. Its common occurrence promises a long and useful life, but thus far, its peculiar properties have not suited specific requirements. It will be interesting to watch its development. Can it possibly go through any such varied and complex series as iron has experienced, for example? At one time there was only a single kind of iron. It met the needs of the time. Later, we find the uses distributed over what was called cast iron, wrought iron, and steel. Then several entirely different cast irons and wrought irons appeared, each of which filled some particular use. Among the steels there are already a myriad of varieties. The carbon steels, which, for a long period of time, were the only steels, are now overshadowed by the special alloy steels, and it seems as though there would be no end to this development. Nickel steels find use in armor plate. Tungsten and chromium steel is the leader in high-speed cutting tools. Molybdenum steel makes most useful permanent magnets for electric meters. Silicon steel fits best the demands of electric transformers, because of its low magnetic hysteresis and high resistivity. Titanium steel is said to be superior for railroad rails. Vanadium steel is apparently particularly valuable for springs, and thus the list grows. All of these alloy steels are the product of the last quarter century, and it is perfectly evident that with the introduction of electric furnaces, the special steel alloys are bound to be still further developed.

W. R. WHITNEY.

HEAT TRANSFER.

In view of the fact that heat transfer apparatus, including all forms of boilers, evaporators, condensers, liquid and gas heaters and coolers, represent so much greater engineering and industrial investment yearly than heat-transforming apparatus like the steam engine and gas engine proper, that there is so little information on the laws of heat transfer, fundamental to the design of the former while numberless books are full of discussions of the laws of transformation supposedly fundamental to the design of the latter, great sums of money are yearly spent in improvement of engines, but very little has been done to increase the capacity of heat transfer surfaces to reduce the size of evaporators, condensers, heaters and coolers. That possibilities of great improvement exist is apparent from the following review. It seems almost axiomatic to say that the rate of heat flow from a region of high temperature to one of low is directly proportional to the difference between those temperatures, and, therefore, that a coefficient generally designated as U will represent the B. t. u.'s transmitted per square foot per degree per hour should have a constant value. How strange it is then to find that the value of U when derived from experimental or engineering practice is found to vary from less than 2 to nearly 1000, with no adequate explanation. The values of $U = 1.8$ are

found in refrigerating rooms with still air when either ammonia or brine is in the pipes, and this value is increased to perhaps 5 or 6 by a vigorous circulation with air velocities up to 900 feet per minute. On the average, however, for these refrigerating pipes, absorbing heat from and giving it to either liquid brine or evaporating ammonia, the value $U = 2.5$ will be found representative. This is very close to the common value of $U = 2$ for steam radiators where heat is passing from condensing steam to mildly circulating air, and likewise, close to the values for steam pipe condensation which lie between $U = 2.5$ and $U = 4.0$, depending on quite a variety of conditions, such as material, color, surface conditions, steam pressure and air circulation. When the heat passes from products of combustion to steam in steam superheaters, the average value is about $U = 4$. Economizers have values lying between $U = 2$ and $U = 3.5$, depending on circumstances and about the same order of magnitude is found in steam boilers which, however, are somewhat different on account of direct radiation influences.

In tank brine coolers where the evaporating ammonia absorbs heat from sluggishly circulating brine in the tank covering the pipe coils, the value $U = 10$ is about right when the vapor leaves the coil reasonably dry. This, however, rises to about $U = 14$ when the coil is flooded with ammonia, compelling the vapor bubbles to pass through liquid to the end of the coil. With double pipe brine coolers, evaporating ammonia absorbing heat from circulating brine, the coefficient is higher and will lie between $U = 30$ and $U = 50$ for velocities between 100 and 200 ft. per minute. A similar range is found in liquid heat exchangers of absorption refrigerating systems, the value being between $U = 50$ and $U = 60$, depending on the velocity, the latter figure corresponding to a velocity of 650 feet per minute. This value of $U = 60$ is common to other apparatus involving the passage of heat from liquid to liquid or liquid to evaporating liquid. It applies directly to water and beer coolers, the liquid trickling over pipes with ammonia evaporating inside. When, however, the heat transfer is from liquid outside to circulating brine inside, it rises to $U = 75$. The absorbers of ammonia vapor where the absorption takes place inside and the aqua ammonia is cooled by water inside, the value is again $U = 60$. The same value applies to open-air ammonia condensers with heat flow from condensing ammonia to water trickling over the outside of the coils. Shell type brine coolers and condensers in which brine or water is circulated through coils, and ammonia evaporated or condensed between coil and shell have a coefficient about $U = 100$. Steam surface condensers similarly constructed have values between $U = 130$ and $U = 200$, depending somewhat on the water velocity, freedom from air and ratio of circulating water to steam. A commonly used value is $U = 180$, reported long ago by Loring and Emery. This same value is used in and found to apply well to some forms of feed-water heaters in which the transfer is of the same class as the sur-

face condenser, *i. e.*, heat flow from condensing steam to circulating water, but recent tests of feed-water heaters show the same peculiarity as was mentioned in the case of double pipe brine coolers—a rise of the coefficient with water speed to values close to $U = 1000$, although few designers would think of exceeding $U = 350$ for these heaters. Passage of heat from condensing liquid to boiling liquid at lower temperature is a characteristic of evaporators of single and multiple effect, and for these $U = 300$ is a fair average value. It is interesting to note that this same value also applies to the generators of absorption refrigerating machines where the heat of condensing steam is given up to rich aqua ammonia liquor.

There is probably no single class more interested, consciously or unconsciously, in increasing the effectiveness of heat transfer surfaces than chemical manu-

facturers, and there is likewise no class with the opportunities for securing the great mass of data necessary for the formulation of laws of design with equal ease. There is presented in this issue a paper on the subject, discussing the various physical constants involved, which, while it leaves much to be said on the subject, will serve to open a thorough investigation of it in these pages. It is hoped that all the users of heat transfer apparatus will send in letters and criticisms of this paper, possibly preparing additional papers, but more important than all else, large quantities of data on every form of heat transfer apparatus in their establishments, all of which we will undertake to print as part of a campaign of improvements that is needed at least as much, if not more, than any other single thing common to all interests.

C. E. LUCKE.

ORIGINAL PAPERS.

HEAT TRANSMISSION.

By HAROLD P. GURNEY.

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It is the purpose of this paper to evolve and present a rational method of analyzing problems in heat transmission along the lines laid down by such eminent and practical authorities as Hausbrand,¹ Mollier,² and Berlowitz.³ The study of the flow or transmission of heat has important bearings in mechanical, electrical, and chemical engineering, and it is a subject which merits a more systematic treatment than is usually accorded to it.

The usual technical case of heat transmission is where heat flows from a relatively hot fluid through a separating plate to a cold fluid. The fluids are usually air, hot gases, water, or steam; in chemical work, the number is almost without limit. The plate is usually thin and of metal, and may be flat, spherical, or tubular in shape. Either or both fluids may be moved parallel or perpendicular to or against the plate, or portions of the plate.

In heat flow, the temperature gradient may be defined as the rate of change in temperature with respect to distance in the direction that the heat is moving; in ordinary units, it is the drop in Fahrenheit degrees per linear inch in the direction of heat flow. When heat is moving uniformly from fluid to fluid through a plate, the temperature gradient is constant throughout the plate. Here the temperature gradient is determined by the rate of heat flow which is constant, and the heat conductivity (or resistivity) of the plate material. In the fluid, the temperature gradient is not constant, it is a maximum at the boundary surface and drops off as the distance from the boundary or plate surface increases. In an infinitesimal film just next to the plate, the temperature gradient is determined solely by the rate of heat flow and by

the true conductivity of the fluid. Beyond this, heat flow results not only from true conductivity, but also from actual transportation of portions of the fluid in the direction of heat flow. This is called convection and it is the heat-transporting power of the fluid. The convectivity of a fluid at any point depends on: (1) the increase in density of the fluid per unit change of temperature, (2) the density, (3) the viscosity, (4) the mean distance from the fluid boundary, and (5) the velocity. It may further be observed that in the plate, the heat flow is constant, whereas in the fluid, the heat flow is greatest at the surface of the plate and diminishes to nothing at a point or points farthest from the plate.

From a practical point of view, it is usual to consider an abrupt drop in temperature from the plate surface to the fluid to exist, and to assume that the fluid has the same temperature throughout. This temperature is the mean effective temperature of the fluid, and, by definition, it is the temperature it would attain if completely mixed without gain or loss of heat. This is a temperature which is different for different parts of an apparatus, and while practically its initial and final values may be readily measured, its intermediate values are obtained with difficulty. For example, the temperature of water circulating through heating coils can be measured before it goes in and after it comes out, but the mean effective temperature at any cross section of the coils is not so easily determined.

Diagrammatically, this discussion may be made clearer by the two following distance-temperature plots. Actually the temperature follows the curve shown in A, but for convenience of treatment, it is assumed to follow the broken curve in B.

This differentiates heat conductivity into two distinct forms: (1) solid heat conductivity where heat traverses a solid or a fluid at rest; and (2) surface heat conductivity where heat passes between a solid and a fluid. The first is the internal conductivity,

¹ Verdampfen, Kondensieren, and Kühlen, 1909.

² Zeitschrift des Vereines deutsche Ingenieure, 1897.

³ Zeitschrift für Apparatentechnik, 1908.

and the second is the boundary conductivity or external conductivity when referred to a plate separating two fluids. The first form of conductivity is a physical characteristic or property of matter. The second form depends not at all on the solid from

The external resistance is the resultant and preceding sum of the boundary resistances of the two sides of the plate. The resistance of a square foot on one side is ζ_1 and on the other side is ζ_{11} ; separate resistances of both sides are ζ_1/A and ζ_{11}/A , and

$$Z_o = \frac{\zeta_1}{A} + \frac{\zeta_{11}}{A}$$

The external resistance of a square foot is z_o

$$z_o = Z_o A = \zeta_1 + \zeta_{11},$$

and

$$Z = \frac{\zeta_1}{A} + \frac{\rho\delta}{A} + \frac{\zeta_{11}}{A}$$

The resistance of a square foot of plate both internal and external is z .

Then,

$$z = ZA = \zeta_1 + \rho\delta + \zeta_{11},$$

and

$$Q = \frac{\Delta AT}{\zeta_1 + \rho\delta + \zeta_{11}}$$

These same facts may be expressed in terms of conductances and conductivities instead of resistances

and resistivities, but it must be observed that where resistances in series are additive, conductances in series are not additive. The resultant of conductances in series is the reciprocal of the sum of the reciprocals of the separate conductances. This results from the fact that conductance is the reciprocal of resistance and is the ratio of heat flow to the temperature drop. If G be used to designate conductance, then,

$$G = \frac{Q}{\frac{\Delta T}{T}} = \frac{\text{rate of heat flow}}{\text{temperature drop}}$$

hence,

$$Q = \Delta TG.$$

The conductance G is the resultant of the internal conductance G_1 and the external conductance G_o .

$$G = \frac{1}{\frac{1}{G_1} + \frac{1}{G_o}}$$

The specific internal conductance or the internal conductivity is the conductance of a portion of plate of one square foot area and one inch thickness and is designated by λ the reciprocal of ρ . Since the internal conductance is proportional to the area of the plate and inversely as its thickness, then,

$$G_1 = \frac{A\lambda}{\delta}$$

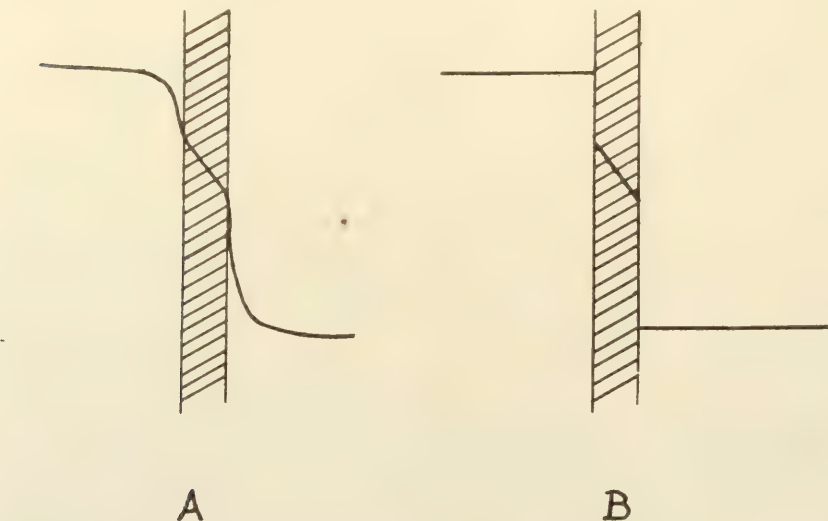
The internal conductance per square foot is g_1 .

$$g_1 = \frac{G_1}{A} = \frac{\lambda}{\delta}$$

The boundary conductances per square foot, or the boundary conductivities are $\gamma_1 = 1/\zeta_1$ and $\gamma_{11} = 1/\zeta_{11}$ and G_o is the external conductance.

$$G_o = \frac{A}{\frac{1}{\gamma_1} + \frac{1}{\gamma_{11}}}$$

The external conductance of a square foot is g_o .



which heat is passing, but on the fluid and especially on such factors as (1) the conductivity, (2) the density and viscosity, (3) the expansiveness to heat, (4) the mean hydraulic radius of the space occupied by the fluid, and (5) the mean fluid viscosity.

In order to investigate quantitatively the flow of heat, a system of notation is here used which is consistently adhered to. Q is the heat units in British thermal units which flow through a heat-transmitting plate in a time T hours, where the temperature difference between the two fluids on either side is Δ degrees Fahrenheit. Z is the heat resistance of the plate. A strict proportionality between the rate of heat flow and the drop in temperature may be assumed. The ratio of the temperature drop to the rate of heat flow may be defined as the resistance, the reciprocal of conductance.

$$Z = \frac{\Delta}{Q}, \quad Q = \frac{\Delta T}{Z}$$

The resistance Z is made up of two separate component resistances: (1) the internal resistance Z_1 of the plate, and (2) the external resistance Z_o , the sum and resultant of the boundary resistance of the plate.

$$Z = Z_1 + Z_o$$

The resistance possessed by a portion of the plate of one square foot area and one inch in thickness is the specific internal resistance or the internal resistivity and is designated by ρ . The area of the plate is A square feet, the thickness is δ inches, and the internal resistance is Z_1 . The plate resistance is proportional to its thickness and to the inverse of its area.

$$Z_1 = \frac{\rho\delta}{A}$$

The internal resistance of a square foot of plate of thickness δ inches is z_1 .

$$z_1 = Z_1 A = \rho\delta$$

$$G_o = \frac{1}{\frac{1}{A} + \frac{\delta}{\gamma_1} + \frac{1}{A_1}}$$

Then the combined conductance G of the plate, both with respect to internal and external conductances is given by the following expression:

$$G = \frac{A}{\frac{1}{\gamma_1} + \frac{\delta}{\gamma} + \frac{1}{\gamma_{11}}}$$

The conductance per square foot is G ,

$$g = \frac{G}{A} = \frac{1}{\frac{1}{\gamma_1} + \frac{\delta}{\gamma} + \frac{1}{\gamma_{11}}}$$

and

$$Q = \frac{\Delta AT}{\frac{1}{\gamma_1} + \frac{\delta}{\lambda} + \frac{1}{\gamma_{11}}}$$

In most heat-transmitting apparatus, the temperature drop is not the same at all points of the drop. The equations deduced hold for infinitesimal plate areas, but by adopting a mean temperature drop in the place of Δ , they may be applied to finite areas. The maximum and minimum temperature differences may always be obtained from measurements on the temperatures of both fluids both before and after transit through the apparatus. The simplest mean temperature difference would be either the arithmetic average, or the geometric mean of the maximum and minimum, but the former is too high, while the latter is too low. The most rational mean is the logarithmic mean and it is obtained by considering the temperature difference to vary relative to time, or distance traversed at a rate proportionate to its instantaneous value. If Δ_o is the minimum temperature difference, Δ_1 the maximum temperature difference and Δ_m the mean temperature difference, then the latter may be expressed in terms of the two former by the following expression:

$$\Delta_m = \frac{\Delta_1 - \Delta_o}{\ln \Delta_1 - \ln \Delta_o}$$

Let the ratio of Δ_o to Δ_1 be a variable, x .

$$\Delta_m = \Delta_1 \frac{1-x}{-\ln x}$$

An arithmetic mean would be $\Delta_1 \frac{x+1}{2}$, while a geometric mean would be $\Delta_1 \sqrt{x}$. The following table brings out the relations between the three means.

x	$\frac{x+1}{2}$	$\frac{x-1}{\ln x}$	\sqrt{x}
1.000	1.000	1.000	1.000
0.900	0.950	0.949	0.949
0.800	0.900	0.896	0.895
0.700	0.850	0.841	0.836
0.600	0.800	0.783	0.775
0.500	0.750	0.722	0.707
0.400	0.700	0.636	0.632
0.300	0.650	0.583	0.548
0.200	0.600	0.497	0.447
0.100	0.550	0.382	0.316
0.050	0.525	0.317	0.223
0.020	0.510	0.251	0.141
0.010	0.505	0.215	0.100
0.000	0.500	0.000	0.000

For design, the use of the geometric mean gives safer values than the logarithmic mean; for investigation, the logarithmic mean should be used. Occasionally, the arithmetic mean may be used.

Where both sides of a plate have the same area as in the case of a flat plate, no doubt arises as to the proper value of A ; but where the areas of both sides of a plate differ as in a pipe, the problem of obtaining a mean area presents itself for investigation. Since the mean heat-transmitting area is nearer in value to the area of the side where there is the greatest heat resistivity, a single mean area may be obtained by weighting the areas with the respective resistivities. The area A_1 has a heat resistivity, ζ_1 ; A_{11} has a heat resistivity, ζ_{11} , and A_m is the mean area.

$$A_m = \frac{\zeta_1 A_1 + \zeta_{11} A_{11}}{\zeta_1 + \zeta_{11}}$$

For a pipe A_o and A_2 being the internal and external areas, Mollier gives the following formula:

$$A_m = \frac{\zeta_1 + \zeta_{11} + \delta \rho}{\frac{\zeta_1}{A_1} + \frac{\zeta_{11}}{A_{11}} + \frac{\rho}{2} \ln \frac{A_2}{A_o}} = \frac{\zeta_1 + \zeta_{11}}{\frac{\zeta_1}{A_1} + \frac{\zeta_{11}}{A_{11}}} \text{ approximately.}$$

A rough rule is to employ as mean area the area whose resistivity is greatest, except where the areas have about equal resistivities, and then an average is quite close.

Apparatus for transmitting heat between fluids may be classified under four types: (1) counter-current, (2) parallel current, (3) perpendicular current, and (4) single current. In counter-current apparatus, the fluids move in opposite directions, and the temperature difference does not generally vary greatly. In parallel current apparatus, the fluids move in the same direction; the temperature difference is at first large and rapidly diminishing, later it is small and slowly diminishing. In perpendicular current apparatus, the fluids move in directions at right angles to each other, and in this respect stands midway between counter-current and parallel current apparatus. In practice, perpendicular current and counter-current apparatus are sometimes placed in series and so become essentially parallel current or counter-current in effect. In single current apparatus, one fluid, and usually the fluid whose temperature it is desired to modify, remains in the apparatus during the entire operation while the heating or cooling fluid moves through at a constant rate. The use of the single current apparatus makes the process intermittent; with other types, the process is continuous.

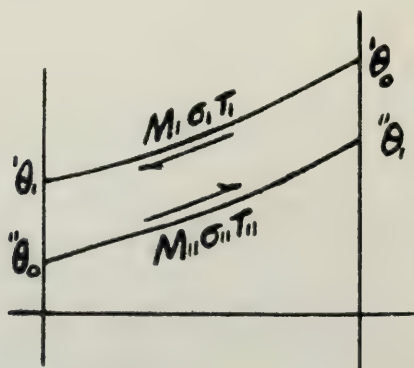
For purposes of investigation and design, all four types of apparatus may be treated in essentially the same manner.

When investigating a heating or cooling apparatus, the initial and final temperatures of both fluids are measured. From this the maximum and minimum, and consequently the mean temperature difference may be obtained. The amount of heat transmitted can be found by multiplying the weight of either fluid into its specific heat, then this into its change in temperature. If necessary, the heat lost in radiation

from the exterior of the apparatus may be taken into account. Knowing the area of the heat-transmitting plate or tubes, all data necessary to compute the heat-transmitting capacity of the walls is at hand.

When designing an apparatus, the heat-transmitting capacity of the plates must be previously estimated from data available or assumed. A preliminary assumption on this point to determine within certain limits the velocities of the fluids, and from this a closer final assumption may be made. The rate at which heat is to be transmitted is obtainable from the weight, specific heat, initial and final temperatures of the fluid whose temperature is to be raised or lowered, and the length of time assigned to the operation. With respect to the fluid supplying heat or cold, its initial temperature and specific heat may be regarded as fixed, but the amount delivered per hour and final temperature are interdependent variables. The most logical starting point in design is to make x a variable ratio of the variable temperature difference to the fixed temperature difference. For any value of x the rate of supply of heating or cooling fluid and the required surface, hence approximate size of apparatus, is easily computed. As x increases, that is, as a larger temperature difference and a smaller temperature change is obtained, the fluid supply rate becomes greater but the size of the apparatus becomes smaller. Against x as abscissae may then be plotted as ordinates the total amount of depreciation, interest, maintenance, and rental on apparatus plus the cost of fluid together with the pumping and storing of the same. The curve obtained will have a minimum, and the best value of x to adopt should be as near to this minimum as possible, at the same time taking into consideration other points of plant economy that would tend to shift this value. In the design of single current and perpendicular current apparatus, two variables similar to x may be chosen instead of one; a simple expedient in these cases is to employ, as abscissae, the products of the two variables and then later try the effect of shifting the ratio of these variables.

Owing to the variety of factors which may come into play, it is not advisable to lay hard and fast rules for the solution of problems in the design of heat-transmitting apparatus. A perfectly general mathematical method might not be at once soundly



theoretical or practical, but a brief outline of the simple mathematical aspects ought to be presented.

Two fluids move counter-current. A weight of hot fluid M_1 of specific heat σ_1 enters at ${}^1\theta_0$ and leaves at ${}^1\theta_1$ undergoing a cooling τ_1 degrees, while a weight of cold fluid M_{11} of specific heat σ_{11} enters at ${}^{11}\theta_0$ and leaves at ${}^{11}\theta_1$, changing in temperature by τ_{11} degrees. When the object is to heat the cold fluid, ${}^1\theta_1$ is a variable and it may be made a function of x by placing ${}^1\theta_0 - {}^{11}\theta_1 = \Delta$ and ${}^1\theta_1 - {}^{11}\theta_0 = \Delta x$.

Then,

$$\Delta_m = \Delta \sqrt{x} \text{ or } \Delta \frac{x-1}{\ln x}$$

$$M_1 = \frac{Q}{\sigma_1(\Delta - \Delta x + \tau_1)} \text{ and } A = \frac{Q}{\Delta_m T_g}$$

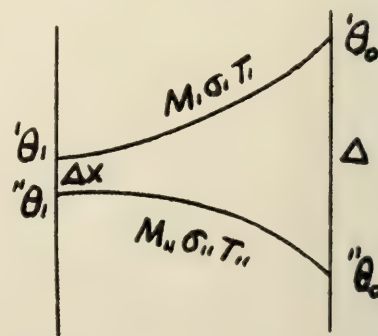
Q is the total heat to be transferred and $Q = M_1\sigma_1\tau_1 = M_{11}\sigma_{11}\tau_{11}$ neglecting outside radiation losses.

When the object is to cool the hot fluid, ${}^{11}\theta_1$ is the variable and $x = \frac{{}^1\theta_0 - {}^{11}\theta_1}{{}^1\theta_1 - {}^{11}\theta_0}$, $\Delta = {}^1\theta_1 - {}^{11}\theta_0$.

Then,

$$\Delta_m = \Delta \sqrt{x} \text{ or } \Delta \frac{x-1}{\ln x}$$

$$M_{11} = \frac{Q}{\sigma_{11}(\Delta - \Delta x + \tau_{11})} \text{ and } A = \frac{Q}{\Delta_m T_g}$$



Parallel current heat transfer is graphically presented above. When the object is to heat the cold fluid, ${}^1\theta_1$ is variable; to cool the hot fluid, ${}^{11}\theta_1$ is variable. Then,

$$\Delta_m = \Delta \frac{x-1}{\ln x}$$

$$M_1 = \frac{Q}{\sigma_1(\Delta - \Delta x - \tau_1)} \text{ or }$$

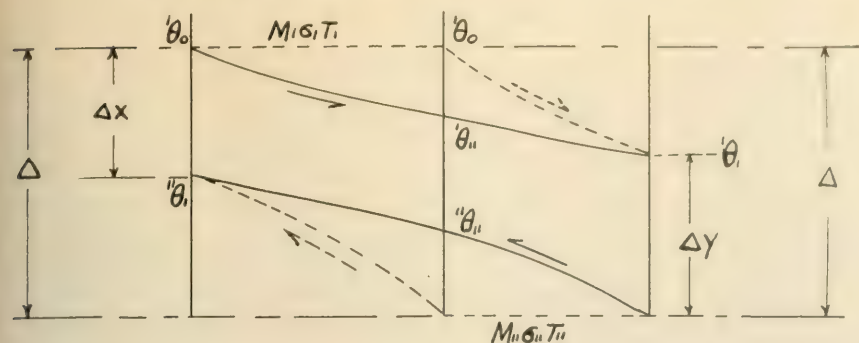
$$M_{11} = \frac{Q}{\sigma_{11}(\Delta - \Delta x - \tau_{11})} \text{ and } A = \frac{Q}{\Delta_m T_g}$$

In perpendicular current heat exchange, a hot fluid of weight M_1 , specific heat σ_1 , enters at ${}^1\theta_0$ and is cooled to a temperature ranging from ${}^1\theta_{11}$ to ${}^1\theta_1$ and undergoing a mean change of temperature τ_1 . A cold fluid of weight M_{11} , specific heat σ_{11} , enters at ${}^{11}\theta_0$ and is heated to temperatures ranging from ${}^{11}\theta_{11}$ to ${}^{11}\theta_1$ and undergoing a mean temperature increase of τ_{11} degrees. As before, $Q = M_1\sigma_1\tau_1 = M_{11}\sigma_{11}\tau_{11}$.

$$\text{Let } x = \frac{{}^1\theta_0 - {}^{11}\theta_1}{{}^1\theta_0 - {}^{11}\theta_0} \text{ and } y = \frac{{}^1\theta_1 - {}^{11}\theta_0}{{}^1\theta_0 - {}^{11}\theta_0}$$

Then,

$$\Delta_m = \Delta \sqrt{xy} \text{ or } \Delta \frac{1-x}{\ln x} \frac{1-y}{\ln y}$$



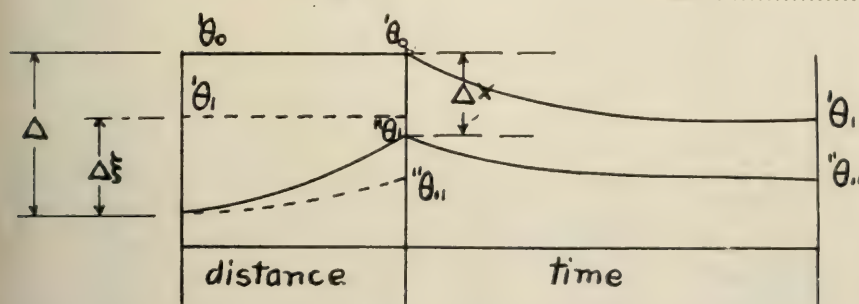
Assuming θ_{11} , θ_1 and θ_{111} straight lines, which is approximately true, then,

$$M_1 = \frac{2Q}{\sigma_1 [\Delta (3-x-y-\frac{1}{2}xy) - 2\tau_{11}]} \text{ or}$$

$$M_{11} = \frac{2Q}{\sigma_{11} [\Delta (3-x-y-xy) - 2\tau_1]}$$

and

$$A = \frac{Q}{\Delta_m T_g}$$



In a single current apparatus for cooling, a hot fluid is cooled from θ_0 to θ_1 . It is here assumed that the temperature of all parts of the fluid that remains in the apparatus during the operation is the same at any time, owing to the use of good stirring devices. The cold fluid enters at θ_0 and is heated at first to θ_{11} , finally to θ_{111} , undergoing a mean temperature rise of τ_{11} degrees. Again, $Q = M_1 \sigma_1 \tau_1 = M_{11} \sigma_{11} \tau_{11}$. Assuming the curve θ_1 θ_{11} a downward parabola, then,

$$\Delta_m = \Delta \sqrt{x\xi} \text{ or } \Delta \frac{1-x}{\ln x} \frac{1-\xi}{\ln \xi}$$

$$M_{11} = \frac{3Q}{\sigma_{11} \Delta (1+2\xi)(1-x)} \text{ and } A = \frac{Q}{\Delta_m T_g}$$

For an extended mathematical study of problems of this type, the reader is referred to papers by M. Berlowitz, "Beitrag zur Berechnung der Heizflächen," *Zeitschrift für Apparatenkunde*, 1908.

In the design of apparatus, no data as to conductivity values is as valuable to the engineer as those obtained by experiment on similar apparatus under exactly the same working conditions. Such data may, however, be found rare, and if all conditions do not coincide, it may be misleading. Such data, if used, ought to be carefully analyzed into its essential parts. In the lack of such data, resource must

be had to what few values, formulae, and rules are extant on the subject, and by careful piecing together of the same, results of no great engineering inaccuracy may be obtained.

The internal conductivity values for different materials has been subjected to much more accurate determinations than boundary conductivities. The internal conductivity is affected by but one variable temperature; the effect of this is but slight, and need not be taken into account.

Below is given a few values of λ and ρ in pound, inch, square foot, hour units.

	λ	ρ
Silver.....	3180	0.00031
Copper ¹	3020-2660	0.00033-0.00038
Aluminum.....	1000	0.001
Zinc ¹	880	0.0011
Tin ¹	435	0.0023
Wrought iron.....	450-420	0.0022-0.0024
Cast iron ¹	490-310	0.0020-0.0032
Steel ¹	320-180	0.0031-0.0056
Lead ¹	230	0.0044
Boiler scale ²	22-8.8	0.05-0.11
Marble.....	14.5	0.07
Glass.....	7.2	0.14
Water.....	4	0.25
Glycerin.....	2	0.5
Alcohol.....	1.1	0.9
Ether.....	0.9	1.1
Oil ²	0.8	1.3
Air.....	0.16	6.3
Carbon dioxide ..	0.1	10

Another table given by Lamb and Wilson may be added, although it corroborates certain values given above.

	λ	ρ
Aluminum.....	995-1005	0.001
Brass.....	590-735	0.0017-0.0014
Copper.....	2085-2095	0.00048
Iron.....	480-470	0.0021
Lead.....	245-220	0.0043
Tin.....	445-315	0.00225-0.00415
Zinc.....	880	0.0012
Clay slate.....	7.9	0.12
Granite.....	14.8-16.0	0.065
Marble.....	13.6-16.3	0.07
White dry sand.....	2.7	0.37
Compact sand.....	1.48	0.68
Plaster of Paris.....	3.7	0.26
Pasteboard.....	1.3	0.77
Fir (along grain).....	0.87	1.15
Fir (across grain).....	0.26	3.9
Hair felt.....	0.31-0.42	2.8
Charcoal.....	0.44	2.3
Silicate cotton.....	0.44	2.3
Brown paper.....	0.48	2.1
Pine shavings.....	0.47	2.1
Air (no baffles).....	0.57	1.75
Pure sawdust.....	0.70	1.4
Dry asbestos.....	0.86	1.15
Sand.....	2.15	0.47

Boundary resistivity is very difficult to express in terms of formulae or equations, owing to the number of factors upon which it depends. The resistivity of a water boundary is usually expressed as a function of the mean velocity of the water where that velocity

¹ *Zeitschrift des Vereines deutscher Ingenieure*, 1876.

² W. Ernst, *Kaiserliche Akademie der Wissenschaften*, 1902.

is artificially impressed, but where the water is "still," it is not so expressed. The resistivity of denser and more viscous liquids is often referred to the resistivity that water would have under like conditions as a standard. The resistivity of an air boundary is also expressed as a function of the mean air velocity, but the air density has a marked effect, close to the inverse of its cube root. As air is usually at atmospheric pressure, this is not taken into account. The heat resistivity of steam is expressed as a function of its mean initial velocity, although its density has an effect much the same as with air. The steam resistivity is not commonly separated from the water resistivity on the opposite side of the plate, and a favorite formula makes the external resistivity a function simply of the plate or tube area. Finally, to allow for incrustation, heat resistance of the metal, oily surface, etc., a factor is often applied to the external resistance. A more rational way is to add the heat resistance of a known thickness of metal, plus the heat resistance of an assumed thickness of scale and oil onto the external resistance.

Between metal and water, the resistivity $\zeta = \frac{0.005}{0.3 + \sqrt{v}}$ [$r = 60 + 200\sqrt{v}$] where v is the velocity of the water in feet per second according to Mollier.¹ When the water is not artificially moved $\zeta = 0.01$ [$r = 100$], although this will be affected by the temperature difference somewhat, owing to induced currents. For water stirred by mixing devices, $\zeta = 0.0025 - 0.0013$ [$r = 400 - 800$]. Ser² places $\zeta = \frac{0.002}{\sqrt{v}}$ [$r = 500\sqrt{v}$], but this gives too high a flow of heat.

The external resistance z_0 of a square foot of plate with moving on both sides is the sum of the separate boundary resistivities.

$$z_0 = \frac{0.005}{0.3 + \sqrt{v_1}} + \frac{0.005}{0.3 + \sqrt{v_{11}}}$$

v_1 and v_{11} are the respective velocities of the water on either side.

To obtain z , the internal resistance of a square foot $\delta\rho + \delta_1\rho_1$ may be added to z_0 , where δ and δ_1 are the thicknesses of metal and maximum allowable thickness of incrustation in inches, and ρ and ρ_1 are the respective resistivities. Practical rules given by Hausbrand³ are that z may be obtained by multiplying z_0 by 1.5 for copper or brass pipes, by 2.0 for iron pipes, and further this should be multiplied by 1.33 where thick liquids are heated, by 1.33 if the surface is oily, and by 1.66 for very thick liquids.

When water is being evaporated by a hot high boiling liquid moving at a velocity v ,

$$z_0 = \frac{0.045}{\sqrt{v}} [g_0 = 22\sqrt{v}].$$

When air is heated by hot water or steam pipes, the air boundary resistance is so large that in comparison the other resistances become negligible;

hence, $\zeta = z_0 = z$. Joule¹ states that $\zeta = \frac{0.55}{\sqrt{v}}$ to 0.47 [$r = 1.8\sqrt{v}$ to $2.1\sqrt{v}$], but the latter values

were no doubt due to radiation. $\zeta = \frac{0.5}{\sqrt{v}}$ [$r = 2\sqrt{v}$] is found to hold good for automobile radiators.

Mollier² proposed $\zeta = \frac{0.89}{0.36 + \sqrt{v}}$ [$r = 0.41 + 1.13\sqrt{v}$].

For sooty surfaces, Hausbrand recommends

$\zeta = \frac{1.77}{0.73 + \sqrt{v}}$ [$r = 0.41 + 0.57\sqrt{v}$] and where the air

is artificially mixed by mixing devices or natural obstructions such as a bank of staggered tubes,

$\zeta = \frac{1.08}{0.45 + v^{\frac{1}{3}}}$ [$r = 0.41 + 0.92v^{\frac{1}{3}}$]. Experiments by

E. Josse, of Charlottenburg, on air moving inside of tubes, give $\zeta = \frac{1.6}{v^{\frac{1}{3}}}$ [$r = 0.63v^{\frac{1}{3}}$] at atmospheric pressure, but with a lower constant for lower pressures.

When air is not artificially moved, the empirical observations of Peclet may advantageously be employed.

The value of r is found to increase with the temperature difference Δ , owing to the higher velocities of induced air currents. For horizontal pipes, where $\Delta = 20^\circ$, the value of r is as follows:

External pipe diameter.....	1/6"	1/2"	1/2"	2/3"	5/6"	1"	1 1/2"	2"	3"	4"
r	0.73	0.57	0.52	0.50	0.48	0.47	0.46	0.45	0.44	0.43

For large vertical surfaces, $r = 0.45 - 0.40$. When Δ is greater than 20° , the value of r may be obtained by multiplying its value at 20° by a factor.

Δ .	Factor.	Δ .	Factor.	Δ .	Factor.
20	1.00	225	1.69	425	1.97
50	1.22	250	1.73	450	2.00
75	1.31	275	1.77
100	1.40	300	1.81
125	1.47	325	1.85
150	1.53	350	1.88
175	1.58	375	1.91
200	1.64	400	1.94

The resistance of a square foot of pipe where heat travels from air through the pipe to air, where v_1 is the velocity of the air inside of the pipe and v_{11} is the velocity of the air outside of the pipe, may be found from either of the following equations:

$$Z = \frac{1.6}{v_1^{\frac{1}{3}}} + \frac{0.89}{0.36 + v_{11}^{\frac{1}{3}}} \quad (1)$$

$$Z = \frac{1.6}{v_1^{\frac{1}{3}}} + \frac{1.08}{0.45 + v_{11}^{\frac{1}{3}}} \quad (2)$$

In (1) the air outside moves parallel to the pipe and in (2) the outside air moves perpendicularly against staggered pipes.

From water to air $\zeta = \frac{1.08}{0.20 + \sqrt{v}}$ [$r = 0.41 + 2.04\sqrt{v}$]

where v is the velocity of the air and the water is broken up into drops as in open-air coolers. When the water is allowed to flow evenly over vertical or

¹ *Zeitschrift des Vereines deutscher Ingenieure*, 1897.

² *Physique industrielle*.

³ Verdampfen, Kondensieren, and Kühlen.

¹ *Philosophical Transactions of the Royal Society*, 1861.

² *Zeitschrift des Vereines deutscher Ingenieure*, 1897.

sloping surfaces $\zeta = \frac{0.75}{0.36 + v} [\gamma = 0.41 + 1.33 v]$.

When the water is still and air passes over it, $\zeta = \frac{0.89}{0.36 + v} [\gamma = 0.41 + 1.13 v]$.

When the water in moist air is partially condensed by cold tubes, the resistance of a square foot z may be obtained by adding the separate resistivities which

are (1) from water to moving air, $\zeta = \frac{0.89}{0.36 + v}$; (2) through water, assuming δ is not greater than $1/10''$ and $\rho = 0.25$, then $\delta\rho = 0.025$; and (3) from metal to the cooling medium, $\zeta = \frac{0.005}{0.3 + v}$ for

water and $\zeta = \frac{1.6}{v_{11}^{\frac{1}{3}}}$ for air.

Occasionally, liquids are cooled by flowing over metallic pipes cooled internally by water. The outside air effects cooling both by assisting evaporation and by conduction. For copper or brass pipes, $z = 0.005$ when the temperature of the liquid to be cooled is above $60^\circ F.$, 0.006 when at $60^\circ F.$ and 0.007 when below $60^\circ F.$ If the metal is iron 0.001 should be added; if the liquid is thicker than water 0.001 , and if very thick, 0.002 should be added. The value of Δ_m in this case is based on the cooling water temperatures.

On the resistivity between metal and steam, experimental observations do not lead to satisfactory formulae. Usually the external resistance of a square foot is given. Experiments by Ser¹ on horizontal tubes with water moving outside at a velocity v_{11} give

$z_o = \frac{0.0022}{v_{11}^{\frac{1}{3}}}$. Joule,² from experiments on a vertical

tube of small diameter, found $z_o = \frac{0.0042}{v_{11}^{\frac{1}{3}}}$. Nichols

found the ratio of z_o of a vertical tube to z_o of a horizontal tube to be $1\frac{1}{2}$, but he obtained a higher value for z_o than Ser. Hagerman⁴ found the rate of heat transmission to depend on the temperature of the water and steam. If t is the steam temperature plus the average water temperature divided by 180, then,

$$z_o = \frac{0.0088}{1 + t} \cdot \frac{0.091}{1 + t + v_{11}}$$

According to the observations of Hausbrand, if v_1 is the mean initial steam velocity, and v_{11} is the mean water velocity, then,

$$z_o = \frac{0.0175}{v_1^{\frac{1}{3}} \cdot 0.023 + v_{11}}$$

To obtain z add $\delta\rho + \delta_1\rho_1$. For iron pipes, multiply by 1.33.

Where water is pumped through coils surrounded by steam, $z_o = \frac{0.0096}{v_{11}^{\frac{1}{3}} \cdot 0.023 + v_{11}}$ where v_{11} is the velocity

of the water; $z_o = \frac{0.04}{v_1^{\frac{1}{3}}}$ to $\frac{0.02}{v_1^{\frac{1}{3}}}$ where liquids are warmed up by steam coils without stirring.

These formulae deal with the resistivity from steam through plates to water which is not evaporating. If the water is boiling, other formulae must be used. Mollier obtained $z_o = 0.0014$, but where rigorous precautions were employed to completely exclude traces of air from the steam, $z_o = 0.0007$. Mollier assumed that the resistivity from metal to water is the same as from metal to steam, $\zeta_1 = \zeta_{11} = 0.00035$. The increased resistance is believed to be due to a film of air. The resistance of a square foot of an air film would be 0.001 on this assumption, and since the heat resistivity of air is 6.25 the film thickness would be $0.0002''$.

From experiments on evaporation, Jellinck¹ proposed the following formula, expressing the resistivity in terms of c the circumference of the steam pipe in feet, and l its length in feet, or A the area in square feet.

$$z_o = 0.00045 c^{\frac{1}{2}} l^{\frac{1}{2}} = 0.00045 \bar{A} \left[g_o = \frac{2200}{1 \bar{A}} \right]$$

Actually, l does not vary as $l^{\frac{1}{2}}$ but as $l^{\frac{1}{3}}$ to $l^{\frac{1}{4}}$. Where l is very large or small this formula does not apply. To allow for incrustation, etc., the following factors of safety are recommended by Hausbrand.²

Ratios of z/z_o	Water.	10-25% solid	Viscous liquids
Copper tubes.....	1.5	2.0	2.5
Wrought iron tubes.....	2.0	2.5	3.0
Cast iron tubes.....	2.5	3.3	4.0
Lead pipes.....	3.0	4.0	4.5

For thick viscous liquids:

$z = 0.075-0.0065$ long heating coils.
 $= 0.0060-0.0055$ short heating coils.
 $= 0.0050$ thin heating coils.
 $0.0070-0.0080$ vertical systems of tubes with steam outside.

In vacuum evaporators, the resistance may become 1.2 to 1.5 times that given above.

In the case of steam-jacketed kettles, if Δ is the temperature difference between the evaporating liquid and the initial steam temperature, then Δ_m should be chosen less than Δ as is given in the following table:

Diameter of kettle.	z_o	$\Delta_m \Delta$
Up to 2 1/2'.....	0.0027	0.85
2 1/2'-5'.....	0.0029	0.80
5'-7 1/2'.....	0.0031	0.75
7 1/2'-10'.....	0.0033	0.70
10' and over.....	0.0035	0.65

For iron, $\frac{z}{z_o} = 1.33$. If there are two steam openings this should be multiplied by $3/4$, for four steam openings multiply by $2/3$, and if a stirring apparatus is used $1/2$ should be used to multiply with.

For vacuum steam-jacketed kettles:

$z = 0.0040-0.0048$ water
 $= 0.0048-0.0055$ thin liquid
 $= 0.0055-0.0100$ thick liquid.

Where multiple-effect evaporators working on liquors presenting no special difficulties, ordinary depths

¹ *Physique industrielle*.

² *Philosophical Transactions of the Royal Society*, 1861.

³ *Engineering*, 1875.

⁴ *Proceedings of the Institute of Civil Engineers*, 1844.

¹ *Zeitschrift des Vereines für Rubenzucker Industrie*, 1894.

² *Verdampfen, Kondensieren, and Kühlen*, 1909.

of liquor being maintained and heated by brass tubes of three feet or over in length, the values of

$$\Delta g = \frac{Q}{TA} \text{ are as follows:}$$

Single effect.....	14000-16000	B. t. u. per sq. ft. per hour
Double effect.....	6000- 7500	B. t. u. per sq. ft. per hour
Triple effect.....	4000- 5200	B. t. u. per sq. ft. per hour
Quadruple effect.....	3750- 4400	B. t. u. per sq. ft. per hour

Where the depth is lower than usual these figures are 10 per cent. higher, wide horizontal tubes 10 per cent. more, narrow, horizontal tubes 15 per cent. more, iron horizontal tubes 10-15 per cent. less, and for evaporators of the spraying or showering types, 10 per cent. more.

THE UTILITY OF THE METALLOGRAPHIC MICROSCOPE.

By JAMES ASTON.

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This article will be confined entirely to the metallographic microscope, without touching upon its use in the immense fields of geology and botany, where the examination of rock sections and vegetable products has a direct utility in engineering. Here, however, the methods are somewhat different than in metallography, since transparent sections and transmitted light (often polarized light) are used. Also, it is not purposed to dwell especially upon the technique of microscopic metallography. The methods employed are presented in good form in several books and numerous articles devoted to the subject. Again no detailed or elaborated discussion of any complex phase of the subject will be taken up. Rather, concrete examples will be brought forward illustrating what metallography has done for us, with the hope that the discussion will open suggestions of its possibilities in individual fields of endeavor.

Metallography is but a step towards the rationalizing of our study of metals and alloys. The earlier work in the study of these materials was naturally along the lines of their possible uses; it consisted of tests of these various properties and a classification according to their several fields of service. A vast accumulation of data of this kind led to the adoption of a rather empirical correlation of composition and quality. Chemical analysis later came in to give us a more exact correlation by the elimination of one big uncertainty, the composition. But chemical analysis falls short of giving us sufficient information regarding our material. Substances owe their properties solely to their make-up, or structure. Composition is but one of the determining factors; chemical analysis therefore fixes but one of the variables. The relation of these chemical elements or the make-up of the material is most vitally dependent on its history. Temperature and pressure conditions, or the proximity of disturbing influences, are of importance. In steels, for example, we consider the effects of heat and mechanical treatment; that is, for identical analyses, a steel annealed at 1200° C. would be weaker than one annealed at 800° C.; one quenched at 800° C. would be harder than the same material slowly cooled from

that temperature, while cast material is weaker than that which has had subsequent rolling or forging.

Structure or make-up is therefore the first step in the interpretation of the properties of materials. An essential in this determination is the composition; chemical analysis is therefore a necessity, and it must be understood clearly that metallographic study is only an auxiliary to the other methods of test. Two lines of attack are open: by the use of the pyrometer and by the use of the microscope. The latter was developed much the earlier, having its beginning in the work of Dr. Sorby in England in 1864 and the later independent investigations of Martens in Germany in 1875. However, the real development has come about within the last ten years; this is due to the rapid progress in physical chemistry, particularly in a better understanding of the theory of solutions. In the earlier work it was possible to develop the structure of the material under examination, but the full measure of the value of the work was missed through the inability to interpret the developments; again systematic research was handicapped by this lack of knowledge. To-day we have a rational interpretation of the results of solidification of molten mixtures and a consequent explanation, more or less developed, of the variations in the structure of alloys occasioned by changes of composition or treatment.

It will be impossible in this paper to dwell upon the use of the pyrometer in the study of the structure of alloys. Cooling curves obtained by its use undoubtedly furnish the most rational basis for the theoretical deductions of the results to be expected on solidification of the melt. But outside of its very direct practical bearing in certain instances, notably in the determination of the critical points of tool steels, the pyrometer may be said in general to be of more scientific interest. The microscope, on the other hand, has a more direct application in the industrial laboratory since with it one is able to make an examination of any desired material as it is used or as it exists, and to interpret from the structure, backed by experience, the condition of the material and its suitability for the purpose in view.

Microscopic examination of metals and alloys is passing through the same cycle that the chemical analysis of iron and steel did some years ago. We have the enthusiast, who would claim for the microscope the power to usurp the functions of other testing methods; and the skeptic, who treats it as a toy and scoffs at any suggestion of utility outside of the laboratory of the scientific investigator. The chief argument of the latter is that the field of view of the microscope is only an extremely small part of a very small sample cut from a large mass of material and it can disclose, therefore, only local conditions. Such argument is hardly tenable; it would apply with equal force to the one-gram sample, the chemical analysis of which controls the 60-ton heat of a steel furnace; or to the purchase of a car-load of coal or a boat-load of ore on determinations of heating value, composition, etc., made on equally small units; or to our methods of design of structures from material whose

strength is taken as that of a small test sample. In fact, all testing methods are based on the principle of a fair average sample of the material under test.

Osmond, the noted French worker, has aptly classed the divisions in the microscopic examination of metals and alloys as anatomical, biological, and pathological. Taking up the last division first, it is needless to point out that the microscope is useful in the detection of incipient cracks and flaws, slag or foreign inclusions, porosities, and the numerous other ills that metals are heir to. Fig. 1 illustrates this point; it is a section of a piece of wrought iron taken perpendicular to the direction of rolling, and shows a slag inclusion. It needs no comment, as it must be very evident that slag particles so breaking the continuity of the metal will have a material effect on the physical properties.

In Fig. 2 is shown a section of a brass casting made in the course of an investigation for a manufacturer who was having trouble with his product. The brasses used were of a composition of about 80 per cent. copper, 10-15 per cent. zinc and 5-10 per cent. lead, the last named being the very common addition agent to brasses to facilitate machining. But brass will hold in solution after solidification only a very small percentage of lead, and any excess will therefore separate out in the free state. This is clearly indicated in the photomicrograph where the free lead is shown in its typical form of black globules. Its effect in machining becomes apparent, since it will break into short chips the otherwise long curling ones of the high copper brasses. On the other hand, it must have equal influence in lowering the strength and ductility of the product; and it is surely not a desirable addition in brasses to be subjected to high temperatures, since the lead will soften or melt at temperatures much below the fusion point of the body material.

Figs. 3 and 4 illustrate a case where the utility of the microscope was rather indirect. Two brass manufacturing concerns A and B were putting on the market a standard article for which there was a large demand. But B's proved stronger than A's and analysis of B's goods indicated the presence of 1 per cent. of iron in the brass. However, when A tried out the new composition it failed to give the strength of B's. Although the compositions are identical the structure differences are pronounced, as indicated in Fig. 3 (of A's) and Fig. 4 (of B's). The coarse structure of A's, together with its marked dirtiness and porosity as compared with the other, led to further investigation, with the final development that the 1 per cent. of iron in B's product had little direct bearing on the strength, and was only that something which was inevitably left behind on the addition of ferromanganese to deoxidize the bath, the manganese being slagged off, and the brass casting left with a clear, fine-grained structure of great strength.

The most work with the microscope has been done in the anatomical division, in the determination of the inner make-up of metals and alloys. Use is made of three facts so fundamental and so vital that they may be presented as axioms.

(1) Metals and alloys are crystalline.

(2) The structure is homogeneous or heterogeneous. Solubility relations govern. It is homogeneous in pure substances, in solid solutions, or in the metallic compounds, and heterogeneous if there is no solubility, or only partial solubility of the constituents after solidification.

(3) The individual melting points of the constituents have no bearing on the order of their crystallization from the melt. The solubility relation of the constituents is again the governing factor.

Fig. 5 is a photomicrograph of Swedish iron and shows the typical homogeneous structure and crystalline habit of a pure metal. The irregular boundaries of the grains are not due to the crystal faces, but indicate rather that crystallization has proceeded from nuclei, or centers, with varying rates of speed, and that the limit of growth has been that due to interference by an adjoining grain. Each grain is a crystalline aggregate of definite crystal system and uniform orientation.

The heterogeneous structure of certain alloys is illustrated in Figs. 6, 7 and 8, the sections being a series of lead-antimony alloys of compositions respectively of 50 Sb, 50 Pb; 13 Sb, 87 Pb; and 5 Sb, 95 Pb. This series is of the type of alloys where the solubility is *nil* after solidification, with consequent complete separation of the constituents as shown, the white being the antimony and the black the lead. In this series, the antimony freezes at 632° C. and the lead at 326° C. and we might expect, therefore, that the antimony would always crystallize out first in a matrix of still fluid lead. This is far from the facts, however, and we see in Fig. 6 the excess antimony crystallizing in a matrix of the eutectic of antimony and lead; in Fig. 8 the lead has solidified first in its typical form in the same matrix as before; while in Fig. 7 we have the eutectic, with its finely divided, intimate mixtures of lead and antimony, due to solidification together at a constant temperature of 228° C. or about 100° C. below the freezing point of the more fusible constituent.

Advantage is taken of this selective crystallization in bearing metals. While suitable bearing metals had been made long before metallography came to our aid, it has pointed out the reasons for success in the use of certain mixtures, and the line of attack necessary in looking for new ones. There are two chief desiderata for a bearing material: First, a low coefficient of friction; this is lowest with the hard metals. Second, plasticity, in order that as unequal wear occurs the pressure of the shaft will squeeze the bearing into conformity and thus avoid local heating by distributing the load equally over the entire surface; this plasticity is obtained with soft materials. Two such opposite properties, hardness and softness, are manifestly not to be obtained by the use of any single homogeneous substance. But by taking advantage of the selectiveness of freezing, we can obtain alloys in which we have a hard constituent bedded in a plastic matrix; the exact nature of the alloy will, of course, depend upon the character of service and the

amount of unit stress on the bearing material. One of our common alloys, Magnolia metal, is of the lead-antimony series, carrying about 20 per cent. of antimony, and consisting therefore of antimony crystals bedded in a plastic eutectic of lead and antimony. Its microstructure would be intermediate between those shown in Figs. 6 and 7.

In Fig. 9 is shown the structure of a Babbitt metal of the copper-tin-antimony series, with two hard constituents, the cubes of SbSn and the needles of SnCu , bedded in the backing of copper.

All of our bearing materials, including Babbitt metals, machinery brasses and bronzes, and cast iron, may be shown to fulfil the conditions laid down above.

In no field is greater use made of the properties resulting from selective freezing than in the ordinary carbon steels. Figs. 10-15 give the structures of several steels with carbon percentages of 0.10, 0.30, 0.60, 0.93, 1.46, and 1.80. We note, as the percentage of carbon increases, that the relative area of the black constituent, as compared to the white, becomes greater, until in Fig. 13, with 0.93 per cent. C., the entire field is occupied by the black constituent. Above this holding of carbon, the white areas increase in magnitude. Structurally, these photomicrographs mean that our slowly cooled carbon steels are heterogeneous, and composed of two constituents, iron (ferrite) and combined carbon (cementite). They are, therefore, made up of an excess substance, either ferrite or cementite, depending upon whether the total carbon is below or above 0.90 per cent., together with the eutectoid of the two constituents, and technically called the pearlite.

In the greatest proportion of commercial steels, with a carbon content below 0.90 per cent., the structure is a heterogeneous mixture of ferrite and pearlite, with the pearlite containing all of the carbon in the form of Fe_3C , the amount of the pearlite increasing as we approach the eutectoid proportion at 0.90 per cent. C. Three facts form the basis of selection of steels of varying carbon percentages for different classes of service; namely, cementite or combined carbon (Fe_3C) is hard, brittle, and of high strength; ferrite, or iron, is soft, ductile and relatively weak; and by shift of carbon composition we can manipulate the relative proportions of these constituents.

In structural steels, with comparatively steady load, we require reasonable strength and elastic limit and high ductility and softness; micrographically, therefore, we need much iron plus some combined carbon, or much ferrite plus some pearlite, which is obtained with a steel of about 0.20 per cent. carbon.

In rails, on the other hand, the load is in the form of a shock, with heavy stresses for short intervals; the requirements are high strength and high elastic limit with reasonable ductility and hardness to resist abrasion. Micrographically this means much combined carbon + some iron, or much pearlite + some ferrite. In open-hearth rails, therefore, we can use steels with carbon from 0.60-0.70 per cent.; but if, because of the irregularities occasioned in manufacture, as in the Bessemer process, we cannot utilize

to the full the properties of the pearlite, we cut the carbon to 0.50 or 0.60 per cent., and reduce the risk of breakage by obtaining higher ductility at the sacrifice of hardness and elasticity.

In line with the above discussion, the microscope shows (Fig. 16) that white cast iron is in reality a very high-carbon steel, with an excess cementite occupying about half of the total field, because of the total carbon content of from $3\frac{1}{2}$ -4 per cent. And we must expect this material to be very hard and brittle and exhibit the silvery fracture from which it derives its name, since the fracture is necessarily along the line of least resistance, or through the brittle cementite areas.

Chemical analysis indicates that gray cast iron differs from the white cast iron not in the quantity of total carbon carried, but because in the gray iron this carbon is largely in the form of free graphite. A simple fracture test shows this, in that a break along the line of least resistance exposes the dark graphite cleavage; hence, the name gray iron. Microscopic examination confirms this, and the distribution of this graphite is shown in Fig. 17 in its typical form as flakes or sheets disseminated throughout the mass of metal. Is it any wonder that cast iron is brittle and weak in tension, when the effective area of the metal is so reduced by the weak plates of graphite? On the other hand, the very thinness of the flakes, while having a maximum effect in lowering the resistance to tensile stress, accounts for the high resistance of cast irons to direct compression. The plates are already so thin that their interposition in the body metal does not result in any further yielding to a direct compressive load.

Except for its free graphite, gray cast iron is seen to be (Fig. 18) nothing more than a steel matrix of high, medium or low carbon, depending upon what proportion of the total carbon has been converted into free graphite because of slow cooling or the presence of silicon or analogous elements.

The microscope is of service in indicating the physical changes taking place in the conversion of hard, brittle white cast iron into the relatively soft and ductile product which we know as malleable cast iron. Due to heat alone (the annealing) the combined carbon is decomposed to iron (ferrite) plus graphite. But since the temperature of annealing is well below that of fusion, the graphite is not free to assume its normal crystalline form (the flake or sheet) and is forced by the comparative rigidity of the metal to assume that shape which will enclose the greatest volume with the minimum of surface. We find the body of the malleable casting to be composed of globules of amorphous carbon bedded in a matrix of iron (Fig. 19). Also, in the usual practice of annealing in mill scale, or its equivalent, the surface layer is decarbonized, to an amount and to a depth depending upon the time, temperature and oxidizing conditions, and appears in the photomicrograph in the typical structure of a carbon-steel. Thus the malleable casting consists of a steel shell of great strength, together with a center of iron in which is embedded graphite in such form as

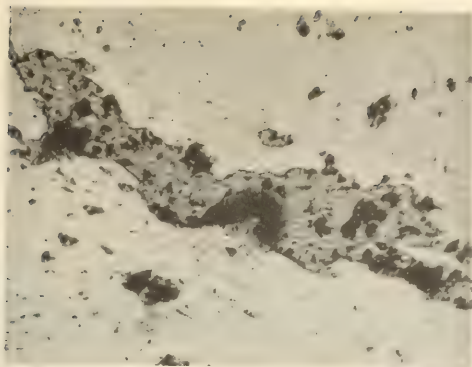


Fig. 1.

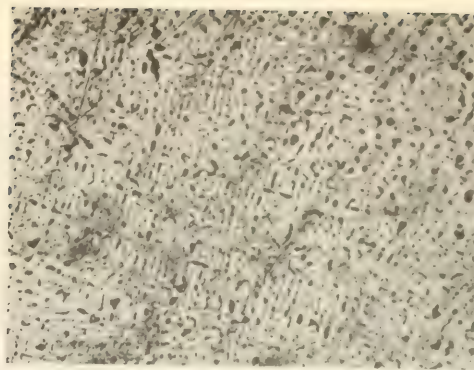


Fig. 2.



Fig. 3.

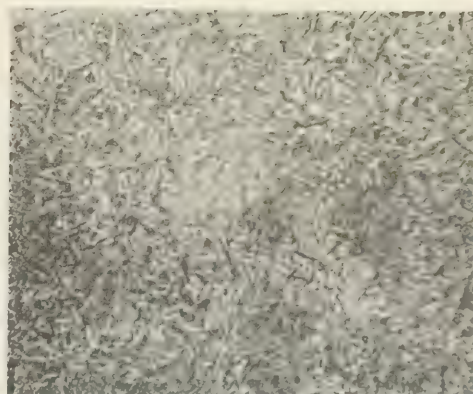


Fig. 4.

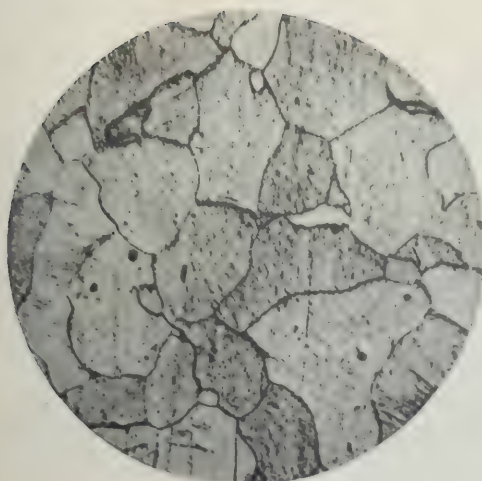


Fig. 5.

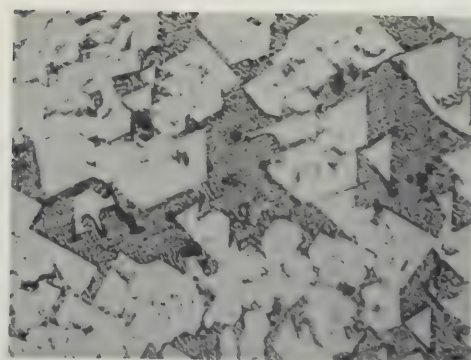


Fig. 6.

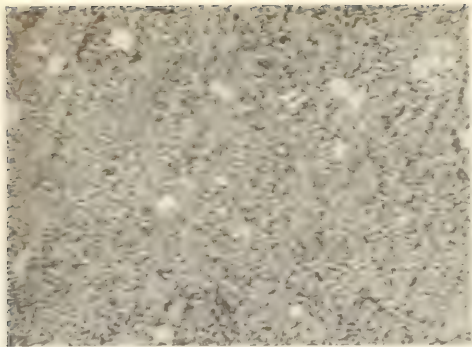


Fig. 7

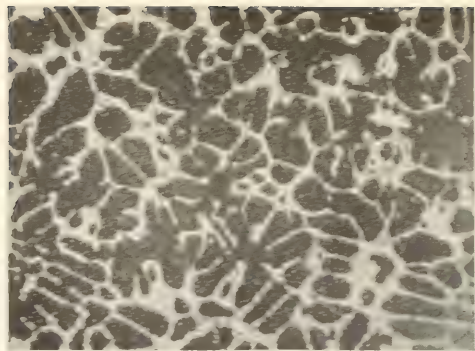


Fig. 8

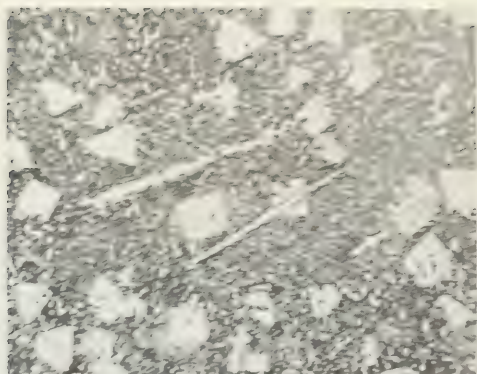


Fig. 9



Fig. 10

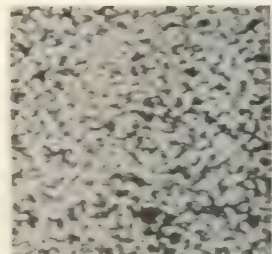


Fig. 11

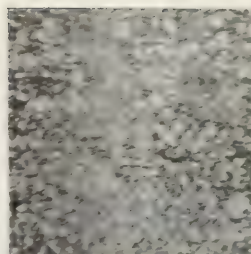


Fig. 12

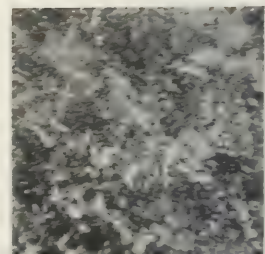


Fig. 13

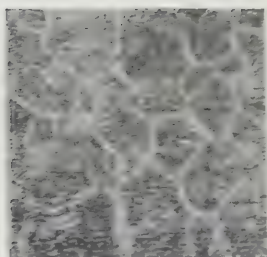


Fig. 14

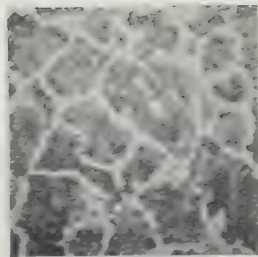


Fig. 15

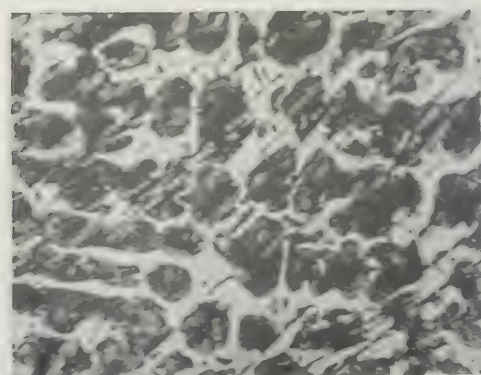


Fig. 16



Fig. 17

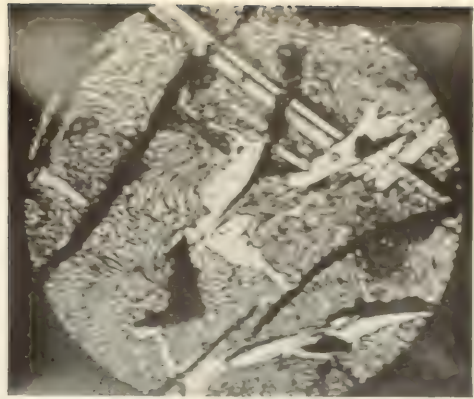


Fig. 18

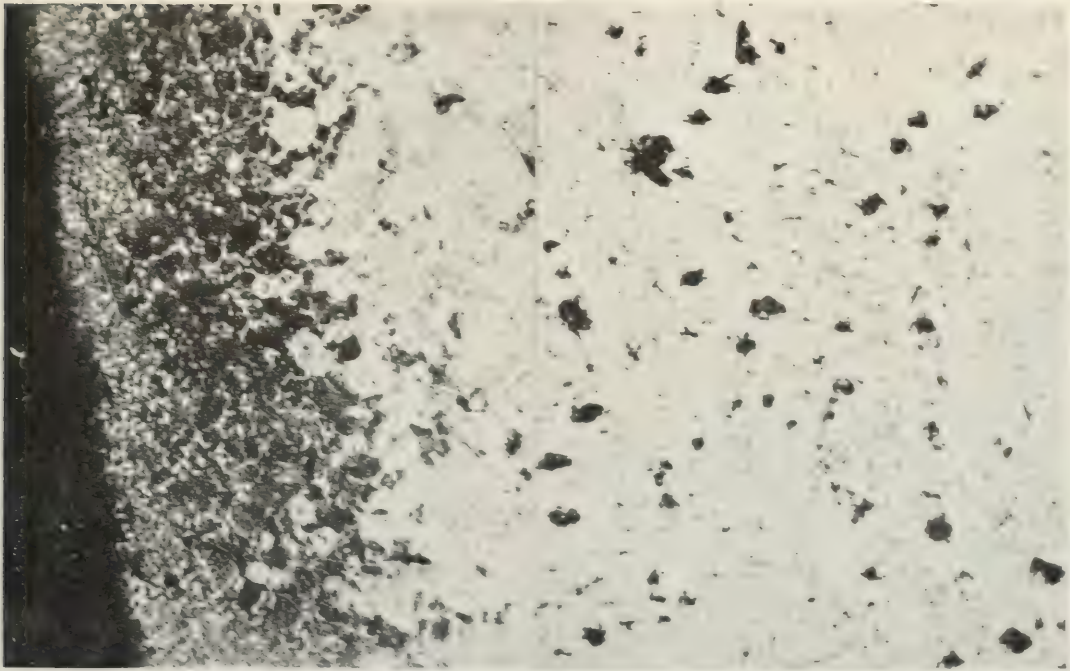


Fig. 19

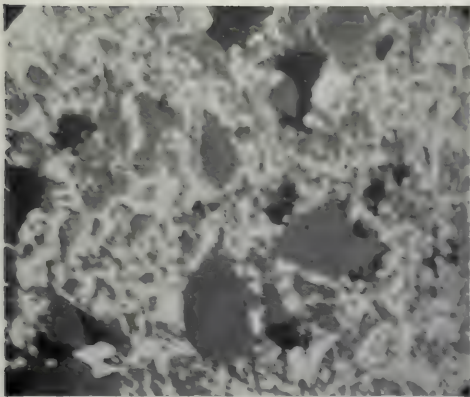


Fig. 20

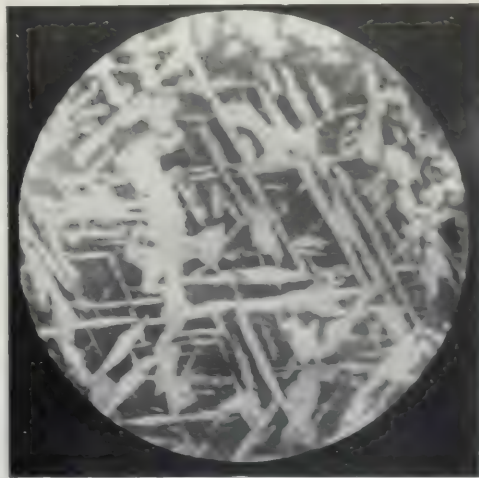


Fig. 21

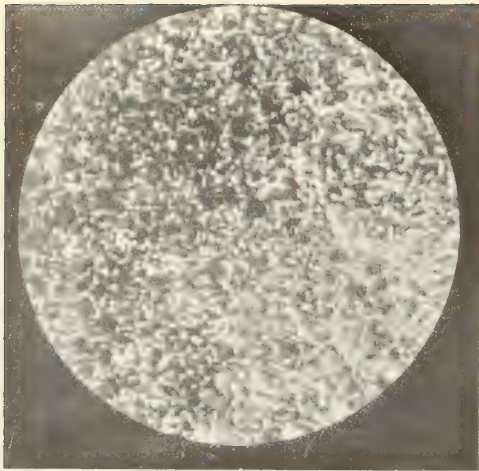


Fig. 22.

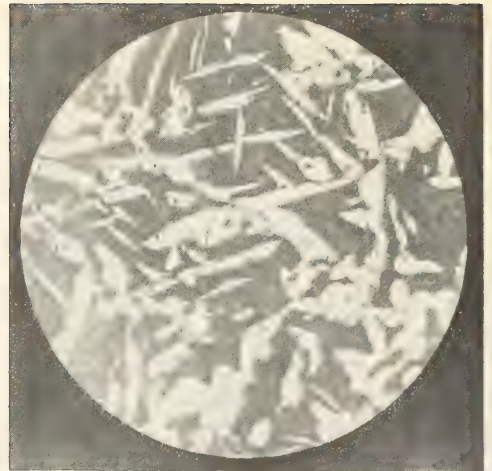


Fig. 23.



Fig. 24.



Fig. 25.

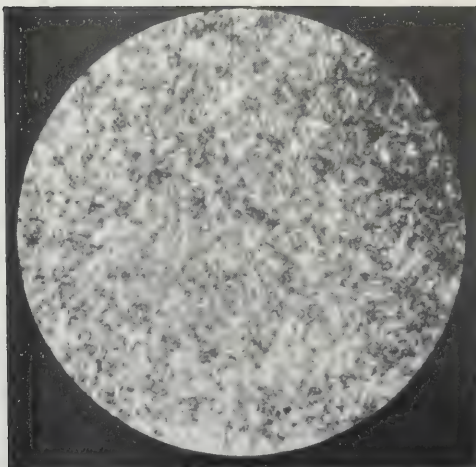


Fig. 26.



Fig. 27.

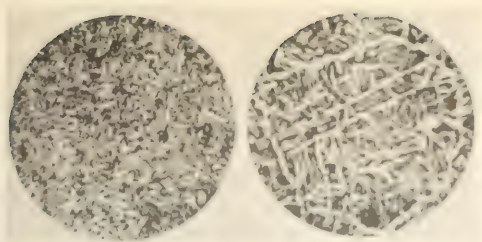


Fig. 28.

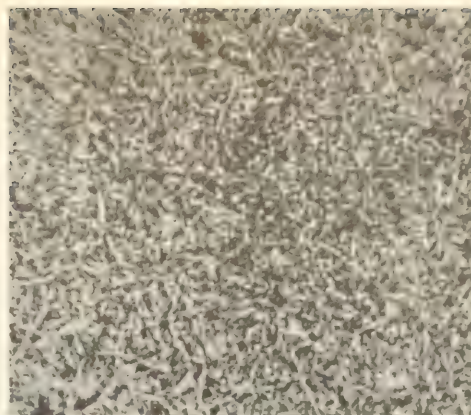


Fig. 29.

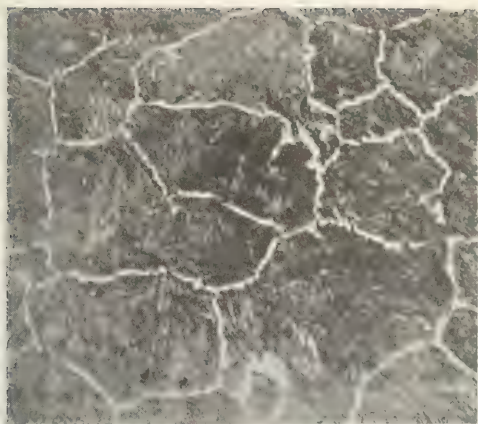


Fig. 30.

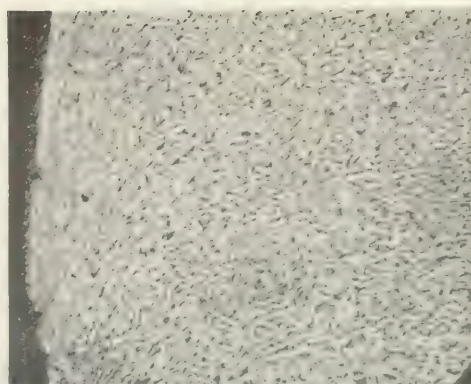


Fig. 31.

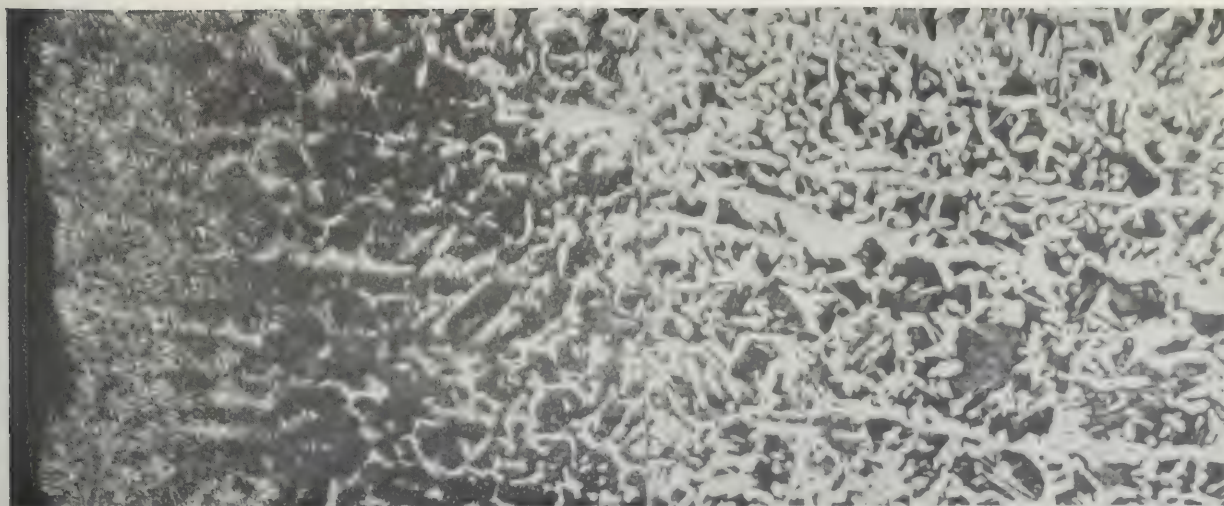


Fig. 32.

to minimize the detrimental effect such as accompanies its crystallization in the normal form appearing in gray cast iron.

In Fig. 20 is shown a photograph to illustrate the utility of the microscope in studying the make-up of materials outside the field of the metals and alloys proper. It is a microsection of a non-metallic base impregnated with a molten metallic compound. The value of the material and its future development depended largely on the nature of the interaction during impregnation. The result might be a single new compound, or two new compounds, or simple solution, or mere mechanical mixture. Chemical analysis proved of little service in this differentiation. But the structure is heterogeneous—this eliminates the single compound or the solid solution. Further microscopic study with selective methods of attack served to identify the constituents and class the product as one of mere mechanical impregnation.

In no field does the microscope become such a useful auxiliary as in the examination of the special or alloy steels; here its usefulness is rather of the future than of the past. It is impossible to dwell upon this phase which is beyond the scope of a paper of this character. It is of interest to note, however, the most important revelation that, in spite of the multiplicity of alloying elements and their various combinations, their influence is largely one of degree and that, after all, the underlying structural considerations are common to all.

While the greatest amount of work of a more scientific nature has been done in the anatomical or structure-composition division perhaps the greatest utility of the microscope in the works laboratory is in the biological division, or that branch correlating the structure changes with the treatment received, for the properties of metals are most vitally dependent upon their mechanical working (whether cast, forged, or rolled) and the heat treatment. Microscopic study, together with determinations with the pyrometer, have given us a rational understanding of the annealing and the tempering of steels. We recognize that the hardening of steels by quenching is due to structural influences occasioned by changes of the relations of carbon and iron; and we can apply this knowledge to advantage in the heat treatment, whereby we can manipulate the properties as desired by taking advantage of the ability to check the structure at any stage between the abnormal one of the quenched state and the normal one of the annealed steel.

One point is vital in this connection and may almost be taken as an axiom. The strength of a steel is inversely proportional to the grain size, and the growth of grain is a result of temperature and time.

Figs. 21-26 are microsections of a steel casting of 0.50 per cent. carbon, and serve to illustrate the marked variations of structure, with consequent changes of physical properties, resulting from heat treatment or mechanical working. Fig. 21 is the steel as cast, with its rather coarse grain due to normal cooling from the high casting temperature. Fig. 22

is the same material after forging, and shows the mechanical breaking down of the grain with a resultant increase of strength. But an annealing of the forged piece at the high temperature of 1100°C . has again (Fig. 23) coarsened the grain, nullifying the effects of forging and leaving the material in no better physical condition than the original casting. A moderate temperature of 800°C ., however, restores the fine-grained structure (Fig. 24). Fig. 25 shows the steel heated to 1000°C . and quenched in water, and gives the typical martensitic structure of a hardened steel. Finally, reheating the material of Fig. 25 to 650°C ., and again quenching, results in the sorbitic texture (Fig. 26), where the transition from the martensitic structure of the hardened steel to the pearlitic structure of the slowly cooled state has been practically completed, but without chance for segregation of the constituents as would be the case if slow annealing had been resorted to. This last figure shows the finest texture it is possible to obtain in steels, and it results, consequently, in the highest combined strength and ductility.

The considerations treated above are of great importance in the control of the annealing and tempering of steels, and have a bearing on the proper finishing temperatures in rolling and forging operations.

In Fig. 27 we have the well-known Roberts-Austen circle, illustrating the marked variations of structure resulting from different heat treatments of a piece of blister steel of 1.50 per cent. carbon, the original structure of which is given in the center.

Fig. 28 is a section of a steel axle broken by fatigue, or continued repetition of stress. The larger grained structure is of the material at fracture, and the fine grain is the result of judicious annealing of the same material. Whether or not the coarse crystallization is the result of the repetition of stress is problematical. It is likely that the original structure in the area of fracture was coarse, favoring therefore the early failure by fatigue because of the more uniform orientation of the crystal cleavages, whereas a fining of the grain by judicious treatment would have resulted in longer life because of a breaking up of the regularity of cleavage directions.

Figs. 29 and 30 are photomicrographs of a steel rail, the former of the original material, with very good grain, and the latter after heating to high temperature. Remembering our axiom regarding the correlation of grain size and strength, it is evident that the heating has resulted in a marked deterioration in quality. These illustrations point out the reasons for the wearing down at the joints of cast welded track, or the weakness of electric welded rail or any welds made without subsequent treatment. The material shown is not burnt, and the structure of Fig. 30 can be changed to one of good quality by proper treatment, either by judicious annealing or, as is the common practice in welding, by hammering or mechanical working of the material.

Fig. 31 illustrates the effect of punching a piece of structural steel. The distortion produced can be traced back from the edge of the hole by the curvature

of the black pearlitic areas in the direction in which the punch was driven through the plate. The depth of distortion depends upon the thickness of the plate and the size (also the sharpness) of the punch; it can easily be measured, and it has been found that for a three-fourth inch hole in a three-quarter inch plate, about one-tenth inch increase of diameter of hole by reaming is necessary to remove all affected material.

Fig. 32 is a section of a steel casting cut by the oxyhydrogen blowpipe. Passing inward from the cut edge, we note the burnt or oxidized portion in the blurred part immediately adjacent; next the enlarged grain of the overheated but not burnt area; then through a gradation of grain size to the normal structure of the interior. This method seems at first sight to have a very detrimental effect, but is in reality slight, since measurement shows a depth of affected material of only four- or five-hundredths of an inch.

Numerous other instances might be cited of the usefulness of the microscope. It has materially assisted in the determination of the nature of the various zinc coatings for the protection of iron surfaces, and we are trying it out in the study of the progression of rusting on metal specimens.

But it will be necessary to conclude with a comment on the probabilities of the future. While the great field of application of metallographic study has naturally been to the metals and alloys, there is every reason to expect extension of its scope to allied lines, such as the examination of complex ores and slags, to ceramic materials and perhaps to coal and coke. In all of these instances we find good and poor materials of identical analysis; the probability is that the interrelations of the constituents are different. An interesting application along this line has just been pointed out in the use of microscopic examination to detect iron blast-furnace slags which are suitable, or otherwise, as a raw material for Portland cement. That vitrification which is essential in the proper slags is brought out very neatly.

Finally we may look to improvement in the microscope itself. We are at present restricted to the study of the heterogeneous structure revealed by ordinary reflected light. The petrographer has the advantage of being able to use transparent sections and polarized light, and in consequence can determine the crystal systems of the constituents of the rock under examination. When suitable apparatus is perfected (it is now being developed) to enable us to determine the crystal forms of the constituents of an opaque specimen by reflected light, then the metallographic microscope will have a materially enlarged scope of application and utility.

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THE SIZING OF PAPER WITH ROSIN COMPOUNDS.

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Received April 10, 1911.

The sizing of paper, from the standpoint of the chemist, is a problem which is not uncommonly sup-

posed to be well understood and fully inquired into, but the true state of the matter is that there is as yet insufficient data available of a nature to determine definitely the actual agencies which perform the function of sizing paper, in confirmation of which be it said that the question has but to be raised to at once introduce a variety of argument and diverse opinions.

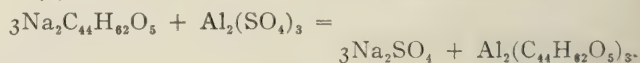
Since the publication of Dr. Würster's treatise on rosin-alum sizing in 1878, our knowledge of chemistry, relating to paper-making, has largely increased, and it is the object of the authors of the present paper to endeavor to summarize the present position of the science, by setting out the results of recent exhaustive researches, in company with a complete criticism of data thereby accumulated, more particularly in connection with the various points concerning rosin sizing, which have long occupied the attention of paper-makers, and paper mill chemists generally.

In turning to consider the present time work and views of leading chemists dealing with the science of paper-making, the question which presents itself at the outset is the selection of a fitting subject-material, but it is obvious that in a treatise of this description the essential contents will imply so much of chemistry as is indispensable for the practical investigation, particular stress being laid upon the coöperation of the practical and theoretical issues, which in the past have remained more or less independent one of the other.

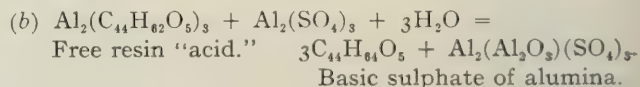
In viewing a scheme of this character it becomes clear that in the theoretical treatment of the chemical processes, which in many ways constitutes the most important part of the problem, the chief considerations are: firstly, the composition and properties of the actual sizing agents (*i. e.*, the products of interaction between rosin size and alum and auxiliary precipitants); secondly, their relationship to cellulose itself.

The present generally accepted theory of sizing action assumes that on the addition of alum the following reactions take place:

(a) (Normal action with theoretical alum.)



Since, however, the quantity used in the mill is much greater than this proportion, the excess is supposed to decompose the neutral resinate of alumina with liberation of the free acid, according to the following equation:



To proceed, Dr. Würster, from the results of his original experimental work, took exception to the then current view (which it may be remarked has till now remained unsettled) that the actual sizing agent is a resinate of alumina, formed as above represented, and asserted that the free rosin acids were the active sizing agents. He drew his conclusions from the results he obtained by extracting rosin-sized

paper with ether and other solvents, the residue, after evaporation, being almost entirely composed of free rosin acids. He also found the alumina in the paper before and after extraction to be the same in amount.

Again, as recently as February, 1907, in *The World's Paper Trade Review*, Mr. Edward F. Moody made the following statement in an article on the same subject—"the free rosin being absolutely insoluble in water is a much better sizing agent than the precipitated and more or less soluble alumine resinate." From a large number of experiments we have found that alumina resinate is very slightly soluble in water at ordinary working temperatures. Mr. Moody further states that "there is no doubt that a pound of free rosin is as effective as two pounds of alumina resinate." Our results do not coincide with this.

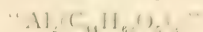
Thus we rapidly reach a fundamental stage in the principles of sizing with rosin soaps. To take the simplest case, What is the best form in which rosin can be applied? One school teaches us that the free rosin is the most valuable constituent of the size—in other words, the more free rosin the size contains, the better the results obtained, upon which theory the custom has developed of making sizes very rich in free rosin, sometimes in the form of an emulsion, containing an exceedingly high percentage of finely divided free rosin particles. On the other hand, some well-known experts maintain that the alum precipitates the size from its solution, producing a complex mixture consisting of alumina resinate and free rosin emulsion. Again, the use of a considerable excess of alum—often more than four times the necessary quantity—is usually recommended. Beyond this important stage, except for the suggestion that the requisite excess has been determined rather by experience than by theoretical calculations based upon scientific grounds, nothing more appears to be known.

Having duly considered the various aspects of this extremely important inquiry, we next approach the details of our work and conclusions on the subject. Any attempt to investigate this problem by experiments conducted on finished sized paper alone is to endeavor to do, at least at this early stage, what is almost impossible. Consequently, we have divided the work of this investigation into three entirely distinct sections, *viz.*: *a* the theory of the constitution and general properties of the active sizing agents; *(b)* their reactions under the influence of varying conditions in the beating engines, more especially with regard to their ultimate sizing efficiency; *(c)* the behavior of cellulose towards such substances, with observations on the deviations from simple additive relations. In the first place, therefore, we will consider the question of the composition and activity of alumina resinate.

In order to isolate the resinsates of alumina, the neutral brown size is dissolved in luke-warm water, diluted to a convenient bulk, and the molecular proportion of pure alum, previously dissolved in water, is gradually added to the solution. The compound resinsates of alumina, which soon separate, are collected

and rapidly washed with water, until the washings no longer contain salts of sulphuric acid.

The air-dried substance has the approximate composition (mean result of twenty-five determinations),



1.000 grams of anhydrous alumina resinate gave 0.0456 gram alumina, Al_2O_3 .

$$\text{Al}_2\text{O}_3 = 4.56 \text{ per cent.}$$

The aluminum derivative of abietic acid, $\text{Al}_2(\text{C}_{14}\text{H}_{10}\text{O}_2)_3$, requires $\text{Al}_2\text{O}_3 = 4.94$ per cent.

It will be seen from the above results that the figure for the equivalent of alumina in aluminum resinate is rather lower than that which theory requires for aluminum abietate. Although as a general statement " Al_2H_3 " holds good for aluminum resinate, it must be borne in mind that commercial rosin itself is a mixture of rosin acids and certain other substances, which are not present in constant proportions and have been found on experiment to possess equivalents varying in a greater degree than that which has hitherto been supposed. Consequently, the composition of the mixture of aluminum resinsates produced during the reaction with alum and neutral rosin differs with the type of size used.

The anhydrous compound aluminum resinate consists of an amorphous powder: it is of a light buff color, resembling rosin, but usually much softer. It dissolves very readily in cold benzene and chloroform, and it is also readily soluble in hot acetic anhydride, but it is only moderately and sometimes partially soluble in oil of turpentine, petroleum, ether, acetone, ether and alcohol. The solvent effects of the two latter bodies we have dealt with fully, later.

The alumina resinate melts at $135-140^\circ\text{C.}$, and yields on ignition a mineral ash consisting of alumina, only traces of foreign bases being present.

We propose to show in the following discussion that the absence of alumina in the "ether-extract" of a rosin-sized paper is not direct evidence in support of the claims brought forward by the exponents of the "free-rosin acid" sizing theory. According to Würster's well-known treatise, to which reference has already been made, it is the free rosin acids which are the effective sizing agents. Würster's observations with regard to the extraction and composition of the size obtained from paper with various solvents are perfectly true, and have been repeatedly confirmed during the course of this investigation. The conclusions arrived at, however, are not at all in accordance with the outcome of our present and more expanded inquiry. As far as Würster's experimental determinations go, the conclusions arrived at are natural and in order, but a new factor must now be taken into consideration, which is—that both ether and alcohol readily cause the decomposition of alumina resinsates to take place, even in the bone-dry condition, the solvents removing some of the products of dissociation formed during the rearrangement of radicals, which occurs during what is known as sizing. Moreover, it is to be remembered that in practice the free rosin already contained in the size used will naturally

be found in the contents of the preliminary ethereal extract.

The results of some experimental determinations concerning the action of solvents on anhydrous alumina resinate are given in the following table:

TABLE I.

	Ether.		Alcohol.	
	Per cent. of alumina, Al_2O_3 , in residue.	Per cent. of alumina, Al_2O_3 , in extract.	Per cent. of alumina, Al_2O_3 , in residue.	Per cent. of alumina, Al_2O_3 , in extract.
1.....	6.01	1.38	5.40	1.71
2.....	6.51	1.28	6.92	1.52
3.....	6.78	1.25	6.40	1.68
4.....	7.40	1.33	8.72	1.41
5.....	6.66	1.30	6.62	1.51

Alumina resinate was shaken up in the cold with excess of ether and allowed to stand for about half an hour. The filtrate was then decanted off and the residue dried. The filtrate was in turn evaporated to dryness and both extract substances analyzed for alumina.

The above preliminary tests led to the quantitative investigation of the amounts in which the two extracts are present, with the results given below:

TABLE II.

Exp.	Percentage		Percentage	
	of residue.	of extract.	of Al_2O_3 in residue.	of ash in filtrate extract.
1.....	40.10	59.90	10.40	1.20
2.....	39.40	60.60	9.05	0.67
3.....	33.50	66.50	8.41	1.30
4.....	40.00	60.00	7.41	1.01
5.....	34.15	65.85	6.16	1.27
6.....	37.10	62.90	9.22	1.10
7.....	37.35	62.65	8.30	1.41
8.....	30.00	70.00	9.16	1.06
9.....	33.3	66.70	10.64	0.30
10.....	32.00	68.00	8.80	1.10
11.....	30.50	69.50	9.53	1.02
12.....	35.10	64.90	9.02	0.86

In dealing with the question of the reaction which really does take place between alums and rosin size, it cannot be denied that much confusion is liable to arise, inasmuch as it is a matter of great significance, and of an intricate and complicated nature, such as is rarely encountered in technical investigation. It has been found during the course of the present investigation, that contrary to the general belief, practically no free rosin acids are liberated during interaction with both neutral and excess of alum; that is, provided that there are no active foreign bodies present, such as other metallic salts, and more especially free acid. The last named is an essential consideration, seeing that many technical difficulties, for instance the discoloration and the deterioration of the strength of paper, can primarily be traced to the unfavorable conditions under which it was sized. Up to this point we have assumed that all the alumina molecules attaching themselves to resin acids are held in the ratio of alumina resinate. It is equally conceivable, however, that two units of affinity are united with the resin acids in some cases, and that the alumina resinate may not only be formulated on the basis of the simplest attachment, but that, in others, where a higher alumina equivalent in proportion to the resin acids, is contained a firmer union of these acids with

basic alumina is involved. From the results of a large number of experiments conducted on the precipitation of alumina resinate with neutral alum, and also of excess of alum in various proportions, and further, the influence of acids and alkalies, salts and other alums in these same reactions we have invariably found that aluminum resinate exists in more than one form or condition, and also in conjunction with cellulose itself: hence the observations which we have advanced above, concerning these precipitated mixtures. Reference has already been made to the condition of the anhydrous alumina resinate which remains when the substance dissolved in ether or alcohol is separated. It is evident that some of the sodium resinate contained in neutral size are too weak to react with equivalent dilute solutions of alum, but certain unstable compounds are formed in the presence of the slightest excess of this precipitant. It is in the capacity of these two kinds of substances for uniting to form an active homogeneous compound, or rather, the opportune and consequent effective transformation of the sodium resinate present into certain modifications of resinous compounds, that the real secret of the efficient and perfect sizing of paper lies.

When anhydrous alumina resinate is treated with cold ether (the same applies in a lesser degree to alcohol) for a considerable time, or even extracted in the ordinary way in a Soxhlet separator for about half an hour, it appears to have undergone an unusual process (possibly pre-existent) of dissociation which may be regarded as caused by an uncertain distribution in the first place of the aluminum base between the various resin acids present, especially since the total quantity of the latter is greater than that required for neutralization (see Table II). As regards the properties of the residual compound (aluminum resinate) X: the substance is a hard amorphous body. It has no definite melting point, but shrinks and darkens at a temperature above 300°C . This derivative does not give the (Liebermann-Storch) reaction, acetic anhydride H_2SO_4 , nor is it attacked by any of the usual solvents. Further, it is but little affected by mineral acids. Hot chloroform, however, has the peculiar property of causing this new compound to take the form of a characteristic jelly-like substance.

It seems plain that all available evidence points to the necessity of recognizing the important part played by aluminum resinate during the process of sizing paper. With a view to further justifying a new position, in advocating the value of aluminum resinate as the real sizing agent, the influence on paper of all the existing sizing materials used in connection with engine-sizing have been investigated, and the results obtained are in complete harmony with those previously arrived at.

Before turning to the data derived from the various paper trials some explanation must be forthcoming to account for the behavior of solvents during the estimation of rosin in paper by the ordinary methods. It has long been known that ether alone does not extract all the resin from paper, and the course invariably recommended is to acidulate the ether with

either acetic or hydrochloric acid, in order to permit of complete extraction. It has also been noted by many observers that the partially extracted paper is not altogether absorbent; in other words, not entirely desized. The experimental data collected and summarized in the following table goes to show that the free rosin in paper is not the most important sizing agent. The sample papers used for this research were manufactured from specially prepared stock, with a view to distinguishing between the added rosin and resinous bodies pre-existing in the pulp furnish of the paper. Moreover, the papers were sized with known quantities of certain market brands of rosin soaps.

TABLE III. —TABLE OF EXTRACTS SOLVENT ETHER

Exp.	Description of papers (all unloaded).	Time, Hrs.	Preliminary rosin extract.	Further extract after decomposition.	Acid used.	Total extracted rosin.	Percentage of ether extract under neutral conditions.
1	Imitation parchment	3	1.66	0.47	HCl	2.13	77.93
2	"	3	1.96	0.36	Acetic	2.32	84.40
3	"	3	1.86	0.35	"	2.21	84.10
4	"	3	1.77	0.41	"	2.18	81.20
5	"	3½	1.87	0.22	"	2.09	90.00
6	"	4	1.85	0.23	HCl	2.08	88.90
7	Manila insulating	3	1.92	0.27	Acetic	2.19	89.60
8	"	3	1.89	0.28	HCl	2.17	87.10
9	Brown wrapper sized	5	0.22	0.08	"	0.30	73.30
10	"	3½	0.21	0.08	Acetic	0.29	72.40
11	"	7	0.18	0.07	"	0.27	66.60
12	"	4	0.20	0.09	"	0.29	69.00
13	"	3	0.22	0.09	"	0.31	72.90
14	"	2	0.19	0.04	HCl	0.23	82.60
15	"	3	0.20	0.10	"	0.30	66.60

In all cases the papers extracted according to the column showing results with ether alone were only partially desized and still ink-resisting. Furthermore, according to the existing methods of analysis, a certain proportion of the remaining alumina resins, though their functions are destroyed, are left behind.

It has been shown in the preceding sections, on the basis of many experimental results, that alumina resinate exists in more than one form and much information has been collected towards the solution of these sizing problems from the behavior of the alumina resinate in the nascent state. A careful consideration of the facts pointed out in the following discussion will show that these influences may be regarded from two different standpoints, *viz.*, that of the stable form alumina resinate, and that involving the formation of still more complicated compounds.

The freshly precipitated or hydrated neutral resinate of alumina is readily soluble to a clear solution in the usual solvents. On continued digestion with ether and alcohol, an extremely interesting and important reaction takes place. In the cold, no essential change is noticeable but, on warming, a white flocculent precipitate gradually settles out, which substance, on analysis, is found to be identical in composition with the residue previously obtained by extraction of the anhydrous alumina resinate, already described. It contains a higher molecular proportion of alumina, and the resinous components appear to have under-

gone a change. The substance itself possesses entirely different physical and chemical properties from those of the normal alumina resinate, which at once confirms our previous impression, that either a process of condensation has taken place, or that the molecular relations of the alumina and rosin acids have been submitted to a rearrangement. The fact that the change is accompanied by a kind of dissociation of the resin acids is very significant, and is the opening of an entirely new field of research, on and around the constitution of resin acids.

To resume: we believe that the explanation of many of the vagaries of sizing lies here, and the essential sequence is, therefore, to make plain, by means of data derived from practical experiments and observations, the full effect of sizing agents under all known conditions. The details of the sizing of trial sheets are given in the following table, in condensed form, in order to render results convenient for the purposes of comparison.

NOTES AND OBSERVATIONS.

The trials are numbered approximately in the order of importance which they occupy in this scheme of classification. The majority of the papers of this series were made from bleached sulphite and soda pulp, and subjected, as nearly as possible, to similar treatment in the beaters. "Neutral size" (column 2) refers to a solution of sodium resins, containing no free rosin, while the term "ordinary size" indicates that a stock size, containing about 6-8 per cent. of free rosin, was used.

An explanation of the signs employed in the preceding table are herewith given:

(-) = Extra free beater pulp.

(x) = Extra wet pulp.

The following is a brief summary of the chief deductions made from the results of this investigation.

It is obvious that in making a relative comparison of the respective merits of the two sizing agents which have in the past been considered of primary importance, the part played by "free rosin" can lay no claim to any particular scientific value. The most general conclusion to be drawn is that nascent alumina resinate already fulfils the essential conditions of a true size, and that, both theoretically and practically speaking, the neutral resinate is a highly effective sizing agent. In actual practice the reaction is in accordance with the general rule above stated, the excess of alum required being only slight, in order to counteract the hardness of the water, and any large excess unnecessary. Further, the excess alum has no effect whatever upon the alumina resinate first formed, and the idea that alumina is precipitated by the soda of the rosin soap, when reaction with alum takes place, has nothing to recommend it. It is true that papers made from moderately wet beater stuff possess a natural resistance to water, and when sized with free rosin in sufficiently large quantity they become hard-sized, solely by virtue of a mechanical surface action on the basis of the fact that the heat of the drying cylinders serves to melt together the small particles

TABLE IV.—PAPER TRIALS.

Exp. No.	Material used.		Precipitant.	Quantity.	Size precipitant.	Sizing agent.	Ink-resisting properties.		Effect of the various chemicals on the paper. Remarks, etc.
	Pulp.	Size.					How sized trade terms.	Standard test seconds. ¹	
1	Unbleached soda	Neutral size	Alum	3%	Chemical equivalent	Alumina resinate	Very hard	410	
2	"	"	"	4 1/2%	"	"	"	450	Excellent surface
3	Bleached soda ²	"	"	5%	"	"	Extra hard	Over 1000	"
4	"	"	"	5%	"	"	Hard	205	
5	Unbleached sulphite ¹	"	"	3%	"	"	Medium	45	
6	"	"	"	5%	"	"	"	55	
7	Bleached soda	"	"	5%	Slight excess	"	Hard	200	
8	Unbleached sulphite	"	"	5%	"	"	Medium to hard	120	Loaded with kaolin
9	"	"	"	6%	"	"	Hard	220	Excellent surface
10	"	"	"	3%	Large excess	"	Medium	35	
11	" ¹	"	"	5%	"	"	"	45	
12	"	Ordinary size	"	3%	Chemical equivalent	Alumina resin and free rosin	"	30	
13	Unbleached sulphite	"	"	5%	Slight excess	Alumina resinate and free rosin	Hard	110	Good surface
14	"	"	"	12%	Large excess	"	"	165	Sizing properties are not entirely relative to quantity
15	"	Neutral	Aluminum hydrate	3%	Chemical equivalent	"	Not sized	2	
16	"	"	"	5%	"	"	"	2	
17	"	"	"	5%	Excess	"	"	3	
18	"	"	Nil	3%	Nil	"	"	1	
19	"	Ordinary size	"	6%	"	"	"	4	
20	"	Neutral	Sulphuric acid	3%	3%	Free rosin	"	2	Causes weakening of the pulp
21	"	Ordinary size	"	6%	6%	"	"	7	Brittle and speckled
22	"	Nil	"	Nil	6%	"	Slightly	10	Parchmentized and brittle
23	"	"	"	"	Large excess	"	Not sized	4	General rotting effect
24	Unbleached sulphite	Nil	Alum	"	10%	"	"	2	Hardened
25	"	"	"	"	20%	"	"	3	Hardened
26	"	"	Caustic soda	"	10%	"	"	1	Softened
27	"	Free rosin	Nil	3%	Nil	"	"	4	
28	"	"	"	5%	"	"	"	4	
29	"	"	"	8%	"	"	"	5	Speckled
30	"	Soln. of free rosin in alcohol	"	4%	"	"	"	1	
31	"	"	"	12%	"	Free rosin	Slightly	10	Heavily speckled
32	"	Free rosin	Alum	3%	3%	"	Not sized	5	
33	"	Rosin in alcohol	"	6%	10%	Free rosin	Slightly	15	Speckled
34	"	"	"	12 1/2%	15%	"	Hard	100	Varnished, unevenly sized, and brittle
35	"	"	Sulphuric acid	6%	3%	"	Not sized	5	Speckled
36	"	"	"	12 1/2%	3%	"	Hard	180	Varnished, unevenly sized, and brittle
37	Unbleached sulphite	Free rosin	"	5%	3%	"	Not sized	1	
38	"	Nil	Aluminum hydrate	Nil	4%	"	"	1	
39	"	Free rosin	"	3%	Chemical equivalent one-half	"	"	1	
40	"	"	"	5%	1%	"	"	1	
41	"	Nil	Nil	Nil	Nil	"	"	1	
42	"	"	Froth oil	"	"	"	"	1	
43	Unbleached soda	"	Nil	"	"	"	"	1	
44	"	"	Froth oil	"	"	"	"	1	
45	"	Free rosin	Nil	3%	"	"	"	1	
46	"	"	"	5%	"	"	"	3	Speckled
47	Unbleached sulphite	Alumina resinate (anhydr.) ¹	"	3%	"	"	"	2	
48	"	Alumina resinate (hydrated) ¹	"	5%	"	"	"	3	
49	Unbleached sulphite	Alkaline soln. of alumina resinate	Nil	5%	Nil	"	Not sized	1	Softened
50	"	Alumina resinate (anhydr.) ¹	Alum	5%	3%	Alumina resinate	Slightly	7	Hardened

¹ The aluminum resinate was applied under ordinary conditions. The papers were run off on a model Fourdiner machine, all being of equal thickness, but not glazed or calendered.

of free rosin, forming what may be best described as a varnish, continuously, though unevenly distributed. Moreover, it has been repeatedly stated by a number of observers that free rosin particles are the effective "sizing agents:" consequently, it occurred to us to try the effect of dispensing with the double operation as carried out in our modern beating engines, and going one step further, to use an all free-rosin emulsion in place of the usual high free-rosin sizes. The results of many attempts, however, were unsatisfactory and conclusive.

Under ordinary circumstances, using normal quantities of size, rich in or entirely composed of free rosin, however intimately the free rosin may have penetrated into the fiber, it will not hard-size it.

The conclusions which have been arrived at by the sizing tests on a practical scale, and also those based upon entirely different considerations, *i. e.*, the behavior of alumina resinate itself, seem to be in striking opposition to much of the doctrine hitherto formulated, and we are brought now to the question of the part played by cellulose in the order of reactions in relation to sizing. Now, Messrs. Cross and Bevan (see work 1900, etc.) suggest that cellulose would decompose the neutral resinate by combining with alumina, and also simultaneously with the rosin acids. From this, one may presume that compounds of "cellulose-alumina resinate" may possibly exist, which would conveniently explain away some of the previous difficulties. Experimental work goes to prove to us that, although such compounds undoubtedly exist, they are only formed under certain circumstances, or, one might say, special conditions, which, under the existing "modus operandi" of paper mills, are liable to be overlooked. As a general statement, it is admitted that when the condition of the pulp in the beater is basic the alumina resinate is partially broken up, and the cellulose, when in the right state, displays a strong affinity towards it, the evolved compound becoming more active by virtue of the union of the cellulose with the resinates of alumina. This subject we propose to treat with in detail in a later publication. It is worthy of note that this type of reaction cannot be said to be constant for all varieties of cellulose, as it has been frequently observed that the completeness of the interactions vary considerably with different kinds and conditions of cellulose. The study of the compound celluloses (so far as this investigation has taken us) regarding their reactions with alumina resinate has led to their division into two classes. For example, according to the previous "conditioning" one can obtain two very dissimilar sizing effects on the same pulp, though using exactly the same proportions of size. In one, predominating, the distinctive properties of alumina resinate may be easily recognized. In the other mixture, many of the properties of the chief components are changed, which can beyond all doubt be affirmed to be due to the formation of a new chemical compound. We are thus disposed to consider the distinction between the various mixtures and chemical compounds, produced during the course of engine-sizing, as being only relative to the primary condition of the cellulose.

In conclusion, it can be anticipated from the foregoing remarks that the hope of a speedy and definite settlement of this question will be justified when the chemical changes which take place between cellulose and alumina resinate are more widely known and that the importance of righting these doubtful issues will be recognized.

AYNSOME TECHNICAL LABORATORIES
LANCASHIRE, ENGLAND.
March 29, 1911.

THE CHEMISTRY OF ANAESTHETICS, II: EXAMINATION OF COMMERCIAL OXYGEN.¹

By CHARLES BASKERVILLE AND RESTON STEVENSON.

A critical study of the many chemicals used for anaesthetic purposes and the modern methods of administration involves the use of oxygen. This paper records the results of the examination of commercial "C. P." oxygen of the various kinds procurable on the market, for its strength and medicinal and chemical purity.

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A. BIBLIOGRAPHY.

1. *The Methods of Preparation of Oxygen.*

The alchemists² were probably acquainted with oxygen, perhaps also the Greeks³ in the fourth century, and the Chinese,⁴ long before Priestley's experiments. In 1630, Jean Rey⁵ knew that certain metals, when heated, fix a portion of the air, and in 1674 Mayow prepared oxygen from niter. In 1771, Scheele⁷ prepared a gas by heating several oxides, including the black oxide of manganese, and, at about the same time, Cavendish⁸ studied oxygen. To Priestley,⁹ however, has been given the honor of discovering oxygen as a constituent of the air. Davy¹⁰ and Lavoisier¹¹ later studied the preparation and nature of this gas.

¹ Read at the regular March meeting of the New York Section of the American Chemical Society, 1911.

² Bolton, *Am. Chem.*, **4**, 170.

³ Hoefer, *Histoire de la Chimie*, **2**, 271.

⁴ Duckwood, *Chem. News*, **63**, 250.

⁵ Jean Rey, *Essai sur la recherche de la cause pour laquelle l'estain et le plomb augmentent de poids quand on les calcine*. Bazas, 1630.

⁶ Mayow, Rodwell, *Chem. News*, **8**, 113.

⁷ Scheele, *Chemische Abhandlung von der Luft und dem Feuer*. Upsala u. Leipzig, 1777.

⁸ Cavendish, *Trans. Roy. Soc.*, **56**, 432, **74**, 119, 170, **75**, 372.

⁹ Priestley, *Ibid.*, **62**, 147; **65**, 384; **73**, 398; **75**, 279; **78**, 147, 313; **79**, 7, 289; *Experiments and Observations on Different Kinds of Air*. London, **2**, 29 (1775-1777); **3**, 1; *Experiments and Observations Relating to Various Branches of Natural Philosophy*. London, **1**, 192 (1779).

¹⁰ *Trans. Roy. Soc.*, **101**, 1.

¹¹ *Chem. J. (Crell)*, **4**, 440, **5**, 125. *Chem. Ann. (Crell)*, **1**, 33, 136 (1786); **1**, 354, 441, 528, 550, 552 (1788); **2**, 55, 262, 431, 433 (1788); **1**, 145, 162, 260, 323 (1789); **2**, 68, 145, 433 (1789); **1**, 69, 518 (1790); **1**, 71 (1791); **1**, 29 (1803).

At the present time, there are the following methods of preparation and manufacture of oxygen:

1. *Heating of Chlorates.*—In 1785, Berthelot prepared oxygen by heating potassium chlorate, and, after him, many investigators¹ have studied the reaction upon heating chlorates and perchlorates. Pure oxygen was made by Stas² by heating potassium chlorate and perchlorate, with or without silica, and several investigators³ have devised apparatus for the generation of the gas by heating chlorates.

2. *Heating Chlorates with Various Substances.*—Döbereiner showed that CuO, etc., lowered the temperature of decomposition of KClO₃, and Gay-Lussac and von Humboldt used moistened KClO₃, and showed that the presence of MnO₂ aided the decomposition. Subsequent investigators⁴ have studied the catalytic action of the oxides of all the metals and of such substances as CdSO₄, platinum black, metals, etc. Others⁵ have patented apparatus for generating oxygen by these processes.

3. *From Hypochlorites.*—Dingler, in 1829, made the observation that bleaching-powder, when heated with the oxide of nickel, cobalt, or copper, evolved oxygen, and Mitscherlich, in 1843, made oxygen by decomposing bleaching-powder. Subsequently it was prepared by heating hypochlorites with MnO₂,⁶ with Fe₂O₃,⁷ with platinum black in sunlight,⁸ with BaO₂,⁹ and with CaO,¹⁰ by heating a solution of hypochlorite with substances such as cobalt peroxide¹¹ and H₂O₂Aq;¹² and Jaubert has devised apparatus and prepared oxygen by the reaction with water of pastilles of bleaching-powder mixed with Na₂O₂,¹³ or with the sulphates of nickel, copper, and cobalt.¹⁴

4. *Reaction of Chlorine and Water.*—D. Müller¹⁵ showed that water vapor and chlorine at 120° form O₂ + HCl. Others¹⁶ have studied this reaction and made modifications in the process.

5. *Heating Sulphuric Acid or Sulphates.*—De Luca¹⁷ made oxygen by passing H₂SO₄ over pieces of porcelain in a hot tube; and Deville and Debray,¹⁸ by heating ZnSO₄ and by squirting H₂SO₄ upon red-hot leaves

of platinum or upon pieces of brick; and Archerau,¹ by heating a mixture of sand and gypsum. Archerau studied also the effects of various metallic oxides upon the decomposition of H₂SO₄ to form oxygen.

6. *Heating Various Solid Substances and Mixtures.*—Priestley prepared oxygen from KNO₃ and from MnO₂; Scheele, from HNO₃; Deville, from NaNO₃ and from Ba(NO₃)₂; Webster,² from NaNO₃ + ZnO; Guertler,³ from CuB₄O₇ at 1000°; and Hilpert⁴ obtained slowly a 5 per cent. reduction of Fe₂O₃ at 1350°. Various apparatus⁵ for the generation of oxygen by heat have been devised.

7. *Combustion of Solid Mixtures.*—These mixtures generate oxygen by burning after they are kindled and consist of a chlorate with combustible matter;⁶ of a chlorate and substances such as iron and zinc oxalate;⁷ or of alkali peroxides mixed with hydrated salts.⁸

8. *Reaction of Peroxides with Water and Aqueous Solutions.*—The following reactions may be used as a source of oxygen: MnO₂ or BaO₂ or PbO₂ with acids;⁹ permanganates or dichromates with acids;¹⁰ H₂O₂ + KMnO₄;¹¹ H₂O₂ + K₃Fe(CN)₆;¹² H₂O₂ + ammoniacal CuSO₄ and other catalytic agents;¹³ water + K₂(CO₃)₂ and other "per" salts or salts with H₂O₂ of crystallization;¹⁴ and water + alkali peroxides with which have been incorporated various substances to retard or accelerate reactions or to improve the keeping quality.¹⁵

9. *Electrolysis.*—The production of oxygen in acid and alkaline solutions with iron, lead, etc., electrodes of various shapes, with or without diaphragms, has been studied by many investigators.¹⁶ Hydrogen,

¹ Archerau, *Chem. Centr.*, **36**, 999 (1865).

² J. H. Pepper, *Chem. News*, **6**, 218 (1862); D. Campbell, *Ibid.*, **6**, 268 (1862); Anonymous, *Ibid.*, **6**, 287, 299, 310 (1862).

³ *Z. anorg. Chem.*, **38**, 456 (1904).

⁴ *Ber.*, **42**, 4893 (1909).

⁵ Stedman, Eng. Pat., 4,548, 1896; Sweetzer, Eng. Pat., 6,408, 1896; Riley and Kershaw, Eng. Pat., 24,885, 1898; W. C. Hughes, Eng. Pat., 21,242, 1902; Kamm, Eng. Pat., 7,048, 1902; Ridley, Eng. Pat., 15,000, 1908.

⁶ Cie. Française de l'Acétylène Dissous, French Pat., 332,098, 1903; Jaubert, French Pat., 350,377, 1904; Jaubert, French Pat., 361,522, 1905; Jaubert, French Pat., 361,537, 1905; Jaubert, Eng. Pat., 22,034, 1909.

⁷ C. Zeiss, Eng. Pat., 17,809, 1910; Turner, *Am. Chem. J.*, **37**, 106 (1907).

⁸ Böck u. Wanz, German Pat., 218,257, 1908.

⁹ Scheele, *Chem. Ann.* (Crell), **2**, 229, 291 (1785); J. Robbins, *Chem. News*, **9**, 126 (1864); Boettger, *J. prakt. Chem.*, **107**, 48; Tonneau, *Union Pharm.*, **45**, 304 (1893); Tommasi, *Chem.-Ztg.*, **17**.

¹⁰ Balmain, *Ann.*, **44**, 217 (1842); Guyard, *Mon. Sci.*, Aug., 1882; Riggs, *J. Am. Chem. Soc.*, **1903**, 876.

¹¹ Voracek, *J. pharm. chim.*, **6** (1882); Lindner, *Chem.-Ztg.*, **9**, 776 (1885); Gohring, *Chem.-Ztg.*, **12**, 1659 (1888); Seyewitz and Poizot, *Compt. rend.*, **144**, 86 (1907); Mosler, *Chem.-Ztg.*, **1909**, 785.

¹² Kassner, *Chem.-Ztg.*, **13**, 1302, 1338, 1407.

¹³ Vitali, *L'Orosi*, **1895**, 1.

¹⁴ *Pharm. Zentralh.*, **45**, 705 (1904); E. Merck, German Pat., 213,457 1907; P. Dame, French Pat., 390,520, 1907.

¹⁵ Robbins, *Chem. News*, **9**, 126 (1864); Jaubert, *Compt. rend.*, **134**, 778; Jaubert, French Pat., 340,388, 1904; Foersterling and Phillip, U. S. Pat., 788,256, 1905; Ageron, French Pat., 352,452, 1905; Roessler and Hasslacher Chem. Co., French Pat., 366,524, 1906; Roessler and Hasslacher Chem. Co., French Pat., 366,326, 1906; Walter, *Chem.-Ztg.*, **32**, 1066 (1908); Sarason, Eng. Pat., 23,676, 1908; Sarason, French Pat., 405,644, 1909.

¹⁶ Garuti, Eng. Pat., 15,588, 1882; Latchinoff, Eng. Pat., 15,935, 1888; Habermann, *Z. angew. Chem.*, **1892**, 323; Swinburne, *Inst. of Elec. Eng.*, July, 1892; Garuti and Pompili, Eng. Pat., 23,663, 1896; Hammerschmid und Hess, *Chem.-Ztg.*, **22**, 123; A. Coehn, Eng. Pat., 23,478, 1893; Crepy, *La Rev. Techn.*, July, **1898**, 292; Schoop, *Z. Electrochem.*, **18**, 241 (1900); Schoop, *Sci. Abstracts*, [1] **4**, 76 (1900); Bell, Eng. Pat., 78,146; Siemens and

¹ Buchholz, *J. für Chem.* (Schweigger), **6**, 219 (1817); *Pharmacopée Française*, **1837**; *Pharm. Centr.*, **8**, 591 (1837); Jungfleisch, *Bull. soc. chim.*, **15**, 6 (1871).

² Stas, *Chem. News*, **73**, 15.

³ Tocke, *Ber.*, **17**, 1831 (1885); Sweetzer, Eng. Pat., 12,245, June, 1895; Mangianeli, French Pat., 409,962, March, 1909.

⁴ Lenard, *Compt. rend.*, **41**, 341 (1855); Krebs, *Chem. Centr.*, **41**, 305 (1870); Jungfleisch, *Bull. soc. chim.*, Aug. 4, 1871; Bandrimont, *J. Chem. Soc.*, **24**, 1151 (1871); Bandrimont, *Mon. Sci.*, Nos. 357 and 358, 1872; Stas, *Chem. News*, **73**, 15 (1873); Loewe, *J. Chem. Soc.*, **27**, 1056 (1874); Wiederhold, *Pogg. Ann.*, **116**, 171; **118**, 186.

⁵ Fowler and Grant, *Chem. News*, **61**, 117; Brown and Stedman, Eng. Pat., 21,067, Oct., 1898; Blackie, Eng. Pat., 9,772, April, 1898.

⁶ Keller, *Rep. für Pharm.* (Buchner), **1848**, 48.

⁷ Artlett, *Chem. News*, **12**, 159 (1865).

⁸ Schönbein, *J. prakt. Chem.*, **98**, 76 (1866).

⁹ Zinno, *Les Mondes*, **1877**.

¹⁰ Beltzer, U. S. Pat., 968,528, 1910.

¹¹ Fleitmann, *Chem. News*, **11**, 255 (1865); Bidet, *Bull. soc. chim.*, **45**, 81 (1886).

¹² Volhard, *Ann.*, **253**, 246 (1890).

¹³ Jaubert, Eng. Pat., 11,466, 1901.

¹⁴ Jaubert, French Pat., 325,627, 1902; French Pat., 333,603, 1903.

¹⁵ *Compt. rend.*, **40**, 906 (1855).

¹⁶ Binks, *Chem. News*, **8**, 168 (1863); Tellier, *J. Soc. Chem. Ind.*, **1890**,

²⁴⁶; Charlopin, U. S. Pat., 713,602, 1902.

¹⁷ De Luca, *Compt. rend.*, **53**, 156 (1860).

¹⁸ Deville and Debray, *Compt. rend.*, **1860**.

ozone, moisture and carbon dioxide are the usual impurities.

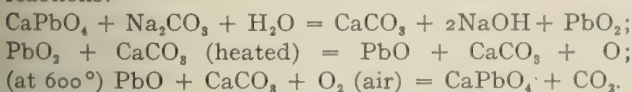
10. *From the Air by Means of Mercury*.—Lavoisier obtained oxygen from the air by formation of HgO by boiling mercury and then decomposing this red oxide by heat.

11. *From the Air by Means of Cu_2Cl_2* .—Mallet¹ found that by passing air over Cu_2Cl_2 with moist sand above 100° , Cu_2OCl_2 was formed; and at 400° , oxygen is evolved and Cu_2Cl_2 reformed.

12. *From the Air, by Means of BaO_2* .—Upon heating BaO_2 , oxygen is evolved and at a lower temperature the oxygen is taken from a stream of air to reform the BaO_2 . Boussingault² and, after him, many others³ have studied this process, devising apparatus and determining the most advantageous conditions of temperature, of pressure, and of the physical structure of the peroxide. Others⁴ have tried the effect of incorporating MgO , CdO , CuO , etc., with the BaO_2 .

13. *From the Air, by Means of Manganates*.—Tessie du Montay⁵ and, subsequently, many others⁶ have studied the production of oxygen by decomposing red hot Na_2MnO_4 by steam and then regenerating it by a current of air at a higher temperature. Various forms of apparatus have been devised and the best conditions of temperature, of pressure, and of the physical structure of the manganate have been determined; and various substances,⁷ such as kaolin, CuO , Na_2SO_4 , NaOH , and MnO_2 , have been incorporated with the manganate to give it a proper physical condition and catalytic activity. Ozonizing⁸ the air has also been tried.

14. *From the Air, by Means of Plumbates*.—Kassner⁹ obtained oxygen from the air by the following reactions:



Obach, Eng. Pat., 11,973; Garuti and Pompili, Eng. Pat., 27,249, 1903; Richards and Landis, *Trans. Am. Electrochem. Soc.*, **3**, 105 (1903); Richards and Landis, *Ibid.*, **4**, 111 (1904); Oerlikon Co., *Electrochem. Met. Ind.*, **1904**, 293; Vaireille, French Pat., 355,652, 1905; L. von Scovay, U. S. Pat., 813,844, 1906; Cowper-Cowles, Eng. Pat., 14,285, 1907; Eycken, Leroy, Moritz, French Pat., 397,319, 1908; Coehn and Osoka, *Z. anorg. Chem.*, **34**, 86 (1903).

¹ Mallet, *Compt. rend.*, **64**, 226 (1867); **66**, 349; J. Phillips, *J. Chem. Soc.*, **24**, 859 (1871).

² Boussingault, *Ann. chim. phys.*, [3] **35**, 5; *Compt. rend.*, **32**, 261, 821 (1851); *J. Chem. Soc.*, **5**, 269 (1852).

³ G. and A. Brin, Eng. Pat., 157; G. and A. Brin, Eng. Pat., 1,416, 1880; Gondols, *J. del'Eclairage du Gaz.*, **1870**, 453; Thorne, *J. Soc. Chem. Ind.*, **8**, 82; Ellice-Plack and Chappman, Eng. Pat., 16,987, 1887; Ellice-Plack and Chappman, Eng. Pat., 1,844 and 3,880, 1888; A. Brin, Eng. Pat., 3,967, 1888; Brin's Oxygen Co., and Murray, Eng. Pat., 14,918, 1893; Price, Eng. Pat., 14,213, 1903; G. von Ach, U. S. Pat., 944,473, 1909.

⁴ Wanklyn, *Polyt. J.*, **213**, 2641 (1872); Gondola, *Compt. rend.*, **66**, 488.

⁵ Tessie du Montay and Marechal, Eng. Pat., 85, 1866; *Chem. News*, **14**, 154 (1866); *Bull. soc. chim.*, **1866**, 398; Tessie du Montay, *Polyt. J.*, **196**, 230 (1868).

⁶ "American Artisan," *Chem. News*, **20**, 44 (1869); Fenta, Eng. Pat., 10,667, 1891; Parkinson, Eng. Pat., 9,457, 1891; Fenta, Eng. Pat., 3,034, 1891; Fanta, *J. Soc. Chem. Ind.*, **11**, 312 (1892); Chappman, Eng. Pat., 19,078, 1892; Lapointe, Eng. Pat., 13,959, 1895; Dutremblay and Lugan, *J. pharm. chim.*, **6**, 392 (1897); Felt, Eng. Pat., 21,299, 1898; Felt, U. S. Pat., 702,855, 1908.

⁷ Bowman, Eng. Pat., 7,851, 1890; Parkinson, Eng. Pat., 14,925, 1890; Webb and Raynor, Eng. Pat., 13,036, 1891; Chappman, Eng. Pat., 11,504, 1892; Hitchcock, *Eng. Min. J.*, **3**, 67 (1899); **4**, 11, 83.

⁸ Lawson, Eng. Pat., 15,998, 1890.

⁹ Eng. Pat., 11,899, 1889.

Plumbates of barium and strontium also were used. Kassner's process was modified¹ to use CO_2 from flue gases, instead of Na_2CO_3 ; and other investigators² have determined the best apparatus and conditions for the process.

15. *From the Air, by Means of Dialysis*.—Graham³ proposed the separation of oxygen by its greater rate of diffusion through colloid septa and through capillaries. Further study⁴ has been made in the effort to adapt this process to commercial use.

16. *From the Air, by Means of Absorption*.—In various substances, such as charcoal, water, alcohol, turpentine, glycerine, naphtha, ether, acetone, chloroform, salt solutions, etc., oxygen is more soluble than nitrogen and can in that way be separated from the air.⁵ Investigators of this process for different solvents and various conditions of temperature, pressure and concentration, indicate that it cannot be applied industrially.

17. *From the Air, by Means of Living Matter*.—Oxygen has been prepared by the natural and artificial respiration of plants,⁶ but not upon an industrial scale. The absorption in blood⁷ has also been studied.

18. *From the Air, by Means of Condensation and Distillation*.—Linde prepared oxygen by the fractional distillation of liquid air. Subsequently, modifications⁸ have been suggested by many investigators, in order to effect a better heat interchange in the distillation and condensation; to use the temperature and energy of expansion and the matter of the residue rich in nitrogen; to employ fractional condensation as well as fractional distillation; and to perfect the mechanical arrangements.

II. Methods of Analysis of Oxygen.

1. *Qualitative Tests*.—The presence of oxygen is shown by these changes: Blue CrCl_2 to green CrCl_3 ; white indigo to blue; colorless NO to brown NO_2 ; darkening of alkaline pyrogallol; white Fe(OH)_2 to blue Fe(OH)_3 , slightly oxidized; blue Fe(OH)_2 ,

¹ Reitz, *J. Soc., Chem. Ind.*, **1890**, 104, 120; **1891**, 71.

² *J. Soc. Chem. Ind.*, **9**, 187 (1890); Langsdon, Eng. Pat., 6,553, 1890; *J. Soc. Chem. Ind.*, **10**, 380 (1891); Kassner, *Polyt. J.*, **204**, 136 (1891); **278**, 468; Kassner, *J. Soc. Chem. Ind.*, **1889**, 885; **1890**, 187; Kassner, *J. Gasbel.*, **34**, 351 (1891); Kassner, *Chem.-Ztg.*, **17**, 1242 (1894); *Compt. rend.*, **117**, 109 (1894); Timm, Eng. Pat., 10,632, 1901.

³ Graham, *J. Chem. Soc.*, **20**, 235 (1867).

⁴ Margis, French Pat., 17,981, 1881; D'Argand, *Bleiblatte*, [1] **31**, 44 (1879); Herzog, *Chem. News*, **59**, 99; Neane, Eng. Pat., 6,463, 1890; Villepigne, Fournier, and Sheuston, Eng. Pat., 19,044, 1896.

⁵ Angus Smith, *Proc. Roy. Soc.*, **12**, 424; Montmagon and de Laire, *Jahresber.*, **1868**, 922; Montmagon and de Laire, *Polyt. J.*, **193**, 434; Mallet, Eng. Pat., 2,137, 1867; Deville and Debray, *Compt. rend.*, **87**, 441 (1878); Helouis, *Ber.*, **1882**, 1221; Reynolds, *J. Soc. Chem. Ind.*, **1890**, 246; G. Claude, *Compt. rend.*, **131**, 447; Bilbie and Wanklyn, Eng. Pat., 8,923, 1899; Brünler, French Pat., 391,213, 1908; Descours-Desacres, French Pat., 396,889, 1908; Levy, Eng. Pat., 5,931, 1909.

⁶ Dutrochet, *Compt. rend.*, **3**, 499 (1836); Schultz, *Ibid.*, **19**, 524 (1844); Boussingault, *Ibid.*, **19**, 945 (1844); Berzelius, *Jahresber.*, **1848**, 267; Boussingault, *Compt. rend.*, **53**, 862 (1862); Böhm, *Biedermann's Centr.*, **1878**, 12.

⁷ Montmagon and de Laire, *Jahresber.*, **1868**, 922.

⁸ Linde, German Pat., 88,824; Schröter, *Engineer*, **1895**, 325; Hampson, Eng. Pat., 7,559, 1896; Thrupp, Eng. Pat., 18,913, 1900; H. A. Strong, Eng. Pat., 9,142, 1900; Le Seuer, Eng. Pat., 4,828, 1901; Pictet, *Engineering*, **1901**, 368; Linde, *Z. Ver. Ing.*, **46**, 1173 (1902); G. Claude, French Pat., 322,702, 1902; G. Claude, *Compt. rend.*, **137**, 783 (1903); Pictet, French Pat., 322,600, 1900; Soc. pour l'exploitation des Procédes. G. Claude, French Pat., 328,245, 1903; Levy and Helbronner, French Pat., 328,770, 1903.

to brownish yellow¹ $\text{Fe}(\text{OH})_3$; turning brown of a solution of NaMnO_4 .² Christomanos³ recommends an ethereal extract of a mixture of $\text{Cu}(\text{NO}_3)_2$ solution + PBr_3 , the ether extract turning green, and the lower layer purple-red.

2. *Determination by Phosphorus*.—Oxygen is accurately determined by the slow combustion of phosphorus.⁴ It has been recommended that⁵ a solution of phosphorus in castor oil, etc., be used, electrically heating the solution for gas mixtures rich in oxygen. Pure oxygen is not absorbed by phosphorus, the absorption beginning at 565 mm. partial pressure and is violent; a gas containing more than 50 per cent. oxygen should not be analyzed by this method.

3. *Determination by Alkaline Pyrogallate*.—Pyrogallol with an excess of KOH absorbs oxygen at all partial pressures readily and accurately.⁶ Its accuracy has been questioned⁷ because of the formation of CO , but this can be prevented by the proper choice of conditions,⁸ particularly by a large excess of KOH .

4. *Determination by Various Methods*.—Priestley's reaction of oxygen with NO was found accurate by some observers⁹ and inaccurate by others.¹⁰

The absorption by freshly precipitated $\text{Fe}(\text{OH})_2$ ¹¹ was considered untrustworthy by Liebig.¹² De Koninck¹³ recommends absorption by an alkaline solution of ferrous tartrate, and Linossier⁴ used this solution with phenosafranine as an indicator.

A solution of Na_2SO_3 ¹⁵ absorbs oxygen and this solution may be titrated by means of ammoniacal cupric sulphate. Mohr¹⁶ questioned the accuracy of this method.

Oxygen is absorbed by solution of $\text{CrCl}_2 + \text{HCl}$,¹⁷ but Berthelot¹⁸ maintains that this solution evolves some hydrogen.

A copper spiral heated electrically,¹⁹ or in any other way, absorbs oxygen, and at room temperature, oxygen

is absorbed by copper¹ with a solution of $(\text{NH}_4)_2\text{CO}_3$ to absorb the CuO which is formed and thus to keep the surface of the copper clean.

Also proposed for the determination of oxygen, is this process:² the gas is mixed in a flask with a solution of MnCl_2 and then $\text{KI} + \text{NaOH}$ are added; the Mn_2O_4 settles out and HCl is added in excess, and the iodine which is evolved is titrated.

B. THE ANALYSIS OF COMMERCIAL OXYGEN.

I. The Methods of Analysis Used.

The following sorts of matter may be suspected to exist in a cylinder of oxygen gas:

1. Solids. 2. Liquids. 3. Gases and vapors: H_2O , halogen acids, HNO_3 , organic acids; O_3 , NO_2 , N_2O , SO_2 ; NH_3 , organic bases; CO_2 , halogens, oxides of chlorine; HCN , $(\text{CN})_2$; PH_3 , SbH_3 , AsH_3 , H_2S ; H_2 , CO , CH_4 , organic matter; N_2 , N_2O , rare gases of the atmosphere.

For these impurities, a qualitative search was first made and then, whenever necessary, a quantitative determination. The following systematic procedure was used:

Experiment (a).

Train:

Cylinder; Trap + red and blue litmus paper and starch-KI paper; P_2O_5 , U-tubes (1) and (2); CaCl_2 tube; moistener + red and blue litmus paper and starch-KI paper; $\text{Ba}(\text{OH})_2$ solution (1); NaOH solution; AgNO_3 solution; 2 CaCl_2 tubes; CuO furnace; CaCl_2 , U-tubes (1) and (2); $\text{Ba}(\text{OH})_2$ solution (2); NaOH tube; gasometer.

By this experiment any solids and liquids were caught in the trap, and the litmus and starch-potassium iodide papers would show the presence of acids, bases, halogens and ozone. The moisture was determined quantitatively by the weighed U-tube containing P_2O_5 on glass wool and the accuracy of this determination was checked by the second weighed P_2O_5 U-tube. The CaCl_2 tube protected the P_2O_5

J. E. Johnson, Jr., U. S. Pat., 783,045, 1905; J. E. Johnson, Jr., U. S. Pat., 933,462, 1905; R. Merves, French Pat., 360,427, 1905; R. Merves, French Pat., 358,236, 1905; Hazard-Flamand, Eng. Pat., 26,720, 1908; Hazard-Flamand, Eng. Pat., 27,592, 1908; Soc. L'Air Liquide, French Pat., 410,967, 1909; Pictet, French Pat., 409,787, 1909; F. Schmidt, French Pat., 403,630, 1909; Janecke, French Pat., 407,852, 1909; Le Seuer, *Met. Chem. Eng.*, **8**, 234 (1910); Röttger, French Pat., 413,958, 1910.

¹ Fuchs, *Am. J. Sci.*, **16**, 397 (1829); cf. Thoms, *Ber. Pharm. Ges.*, **1894**, 240.

² Phillips, *Am. Chem. J.*, **16**, 340.

³ *Verh. Ges. Dcut. Naturf. Aerzte*, **1905**, II, 76.

⁴ Boussingault, *Compt. rend.*, **58**, 777 (1864); Otto Lindemann, *Z. anal. Chem.*, **18**, 158 (1879).

⁵ Centreiszwier, *Chem.-Ztg.*, **34**, 494 (1910).

⁶ Liebig, *Ann.*, **77**, 107 (1850).

⁷ Calvert, *Compt. rend.*, **57**, 873 (1863); Cloez, *Compt. rend.*, **57**, 875 (1863); Boussingault, *Compt. rend.*, **57**, 885 (1863).

⁸ Weyl and Goth, *Ber.*, **14**, 2659 (1882); Clowes, *Chem. News*, **74**, 199 (1896); Hempel's *Gas Anal.*, Dennis, **1906**, 149.

⁹ Wanklyn, *Chem. News*, **62**, 263 (1890); **65**, 49 (1892); Kreider, *Z. anorg. Chem.*, **13**, 418 (1896).

¹⁰ De Koninck, *Z. angew. Chem.*, **1891**, 78.

¹¹ Hart, *Z. anal. Chem.*, **1869**, 482; Mohr, *Ibid.*, **12**, 138 (1874).

¹² *J. Chem. Soc.*, **26**, 935 (1873).

¹³ *Z. angew. Chem.*, **1890**, 727.

¹⁴ *J. pharm. chim.*, [5] **23**, 103 (1891).

¹⁵ Schutzenberger and G6rordin, *Compt. rend.*, **75**, 879 (1873); Schutzenberger and Risler, *Bull. soc. chim.*, [2] **19**, 152 (1873); Graham, *Mem. Chem. Soc.*, **3**, 46.

¹⁶ *Z. anal. Chem.*, **12**, 138 (1874).

¹⁷ Von der Pfordten, *Ann.*, **225**, 112.

¹⁸ Berthelot, *Compt. rend.*, **127**, 24.

¹⁹ F. Fischer, *Ber.*, **12**, 1696; Von Jolly, *Ann. physik. N. F.*, **6**, 520.

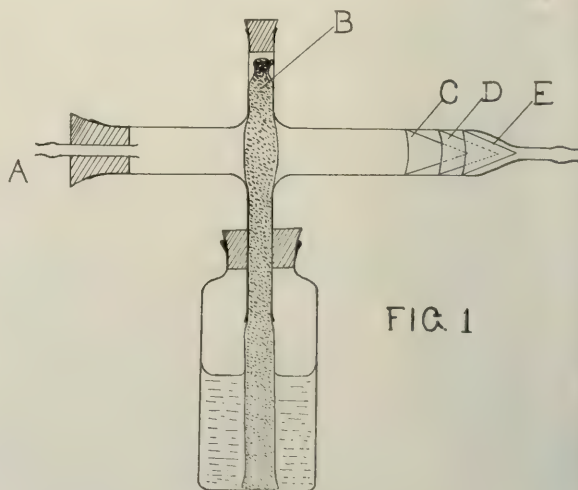


FIG. 1

U-tube from absorption of water from the moistener. This apparatus is shown in Fig. 1. The gas enters at A; it then passes the wet porous cotton rope B

¹ Hempel, *Z. anal. Chem.*, **20**, 499 (1881).

² Winkler, *Ibid.*, **28**, 366 (1889); Chloropin, *Chem. Centr.*, **1899**, i, 372.

which does not contain enough water to absorb the impurities from the gas but does moisten it enough to enable the impurities in it to react with test papers; and then the gas passes through cones *C*, *D* and *E* of litmus and starch-potassium iodide papers, repeating with moistened gas the tests made before in the trap tube. The nearly saturated $\text{Ba}(\text{OH})_2$ solution showed the presence or absence of CO_2 , and after the run, this solution was divided into three portions: the first portion was acidified with HCl and tested for SO_3 ; the second portion with $\text{HNO}_3 + \text{AgNO}_3$, for halogens and halogen acids and oxides of chlorine; and the third portion was set aside. After the run, the NaOH solution (2 : 3) was divided into three portions: to the first portion was added BaCl_2 and then HCl in excess, thus testing for CO_2 , SO_2 , SO_3 ; the second portion was acidified with HNO_3 , then made ammoniacal, AgNO_3 was added and then the solution was made acid with HNO_3 , thus testing for SO_2 , H_2S , halogens, halogen acids and chlorine oxides; the third portion was mixed with the third portion of the $\text{Ba}(\text{OH})_2$ solution (see above) and tested for HCN and $(\text{CN})_2$ by boiling with $\text{Fe}(\text{OH})_2 + \text{Fe}(\text{OH})_3$ and acidifying with HCl to form Prussian blue.

The AgNO_3 solution repeats some of the previous tests and in addition shows the absence or presence of PH_3 , SbH_3 and AsH_3 . The gas is then dried by the two CaCl_2 tubes, and the H_2 and organic compounds are oxidized by the red hot CuO . The water which is formed is weighed in the CaCl_2 U-tube (1), which is guarded by the weighed CaCl_2 U-tube (2); and the CO_2 which is formed is absorbed in the nearly saturated $\text{Ba}(\text{OH})_2$ solution (2). This last tube is guarded by a tube containing solid NaOH . The gas is measured in the gasometer. From 10 to 18 liters of gas were usually passed in from 3 to 6 hours; the separate bubbles could easily be counted.

Experiment (b).

Train:

Cylinder; trap and litmus paper and starch-KI paper; starch-KI solution; FeSO_4 solution, slightly acid; KMnO_4 solution; gasometer.

The trap and test papers used in experiment (a) were again used in this experiment, so that the tests were repeated in an accumulative manner. The starch-KI solution gives a test for ozone, and portions of this solution were tested before and after the run with methyl-orange and phenolphthalein to indicate acids and bases in the gas. The slightly acid solution of FeSO_4 is titrated before and after the passage of the gas to show the presence of active oxidizing agents. Naturally, it would appear that the oxygen gas would itself oxidize this solution, but such is not the case.¹

The KMnO_4 solution, made by adding one drop of $\text{N}/2$ KMnO_4 to 500 cc. of water, tests for reducing agents.

By these two experiments, qualitative tests are made for all likely constituents of the gas, except the following:

¹ The stability of FeSO_4 in solution in the presence of oxygen and air at various temperatures, etc., has been investigated by the authors, *J. Am. Chem. Soc.*, **33**, 1104.

Oxygen, which is determined quantitatively; N_2 and the rare atmospheric gases, which are obtained by difference; and N_2O , for which no sensitive test is known. It is assumed to be absent. Further tests for CO^1 were found unnecessary, since no organic matter was detected, except in one sample, and, in that instance, only a faint trace.

In addition to the quantitative determinations of H_2O and H_2 made in experiments (a) and (b), determinations of CO_2 and O_2 were made as follows:

Experiment (c).

CO_2 was determined by absorption in a NaOH solution (2 : 3) saturated with O_2 , and weighing.

Experiment (d).

The sample of gas was measured over water in an Elliot apparatus consisting of a 100 cc. burette surrounded by an air jacket, CO_2 and oxygen were absorbed by fresh alkaline permanganate, and the gas residue was measured over water in a tube of small bore.

The alkaline pyrogallol was made up according to Hempel,² 5 grams pyrogallol in 15 cc. $\text{H}_2\text{O} + 120$ grams KOH in 80 cc. H_2O . These solutions were mixed and immediately poured into "individual" bottles, each containing just more than enough for analysis. The KOH (c. p. "by alcohol") used for this solution was fused and about 1/20th of its weight of Na_2O_2 added; the temperature of the mixture was raised until oxygen was liberated in abundance and then cooled somewhat; the melt was poured into water which caused the evolution of more oxygen and the solution boiled free of gas. It then contained no alcohol or other organic impurities. Determinations of the CO in several gas residues showed that about 0.05 per cent. CO is formed in this analysis and this amount was added as a correction to the percentage of oxygen.

II. Results of Analysis.

Below is given a tabulation of the results of analyses, according to the methods given above, of seven makes of commercial "C. P." oxygen. The percentages represent the volumetric proportion of the different constituents of the gas just as it emerged from the cylinder and not upon the dry basis.

ANALYSIS.

No.	Source of oxygen.	O_2	H_2O	CO_2	H_2	Organic Matter.	N_2 etc.	All other impurities
1	$\text{KClO}_3 + \text{MnO}_2$	93.20	0.30	0.11	0	0	6.39	0
2	$\text{KClO}_3 + \text{MnO}_2$	98.31	0.14	present	0	0	1.54	0
3	$\text{KClO}_3 + \text{MnO}_2$	92.82	0.26	trace	0	0	6.92	0
4	$\text{KClO}_3 + \text{MnO}_2$	97.13	0.23	present	0	trace	2.63	0
5	Liquid air	96.10	0.15	0.01	0	0	3.74	0
6	Electrolysis	99.23	0.35	0.03	0.14	0	0.25	0
7	$\text{Na}_2\text{O}_2 + \text{H}_2\text{O}$	99.20	0.50	trace	0	0	0.30	0

III. Conclusions.

The seven samples of oxygen examined by us were all medicinally pure. For some purposes they were ready for use, but for calorimetry, elementary organic analysis by combustion, gas analysis, etc., they would have required previous purification or else a correction for the impurities present.

¹ Hempel, *Gas Analysis*, Dennis, 1906, p. 212.

² Hempel, *loc. cit.*, p. 49.

C. STANDARDS OF PURITY RECOMMENDED FOR OXYGEN TO BE USED IN MEDICINE.

The gas should be neutral toward moist delicate litmus paper; and when passed through an aqueous solution of silver nitrate, it should produce no turbidity. Not more than an opalescence should be produced when 2 liters of the gas are passed slowly through an aqueous solution of barium hydroxide. When 5 liters of the gas are passed slowly through an aqueous solution of sodium hydroxide, then over heated copper oxide, and finally through an aqueous solution of barium hydroxide, no turbidity should be produced. The gas should contain at least 94 per cent. oxygen upon the dry basis. As supplied for use, the gas should contain no liquids and no solids.

COLLEGE OF THE CITY OF NEW YORK,
APRIL, 1911.

THE DETERMINATION OF VANADIUM IN VANADIUM AND CHROME-VANADIUM STEELS.

By J. R. CAIN.

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INTRODUCTION.

Vanadium has been called by metallurgists a "homeopathic" remedy because of the remarkable results obtained by small additions of it to other metals, notably to steel. Carbon steels or alloy steels as produced in this country, when they carry vanadium, usually contain from 0.10–1.00 per cent. It has been claimed by some that the element acts by removing dissolved gases, especially nitrogen, from the molten steel, with resulting elimination in the slag of the greater part added, and that the amount left in the steel itself is of secondary importance. However, others have shown that the microscopic structure of steel is greatly modified by the residual vanadium in the amounts in question here, and, as might be expected, there are corresponding changes in physical properties. Hence it will be seen that a high degree of accuracy in determining vanadium in steel is to be desired. Considerations such as these, combined with requests from many sources, led the Bureau of Standards to undertake the preparation of a vanadium standard steel similar to the analyzed plain carbon steels which it has issued for some time. In conformity with the usual practice of the Bureau, samples were analyzed by its chemists and by prominent technical and works chemists (eleven in all). The first figures thus obtained for vanadium were so unexpectedly discordant as to indicate sources of error in methods used which had probably been overlooked or unrecognized. Accordingly, some of the most probable of these were investigated by the Bureau. The results of this investigation were communicated to those participating in the coöperative work, and a satisfactory concordance in the final vanadium figures was very soon obtained. Inasmuch as some of these sources of error do not seem to have been sufficiently emphasized in the literature, concise statements regarding them may be of service. Three classes of methods were used by the coöperating analysts:

Class A.—Methods like that first described by Campagne¹ and found with little variation from the original in many text-books on steel analysis. The hydrochloric acid (ferric) solution of the steel is extracted with ether, which removes most of the iron, leaving the vanadium in the aqueous layer. This portion is evaporated to dryness and the operation repeated two or three times with fresh portions of hydrochloric acid. The latter reduces the vanadium to the quadrivalent state; the final evaporation is made with sulphuric acid and is continued until fumes are given off strongly. The solution is then titrated against permanganate.

Class B.—Methods depending upon the reduction of quinquivalent to quadrivalent vanadium by ferrous sulphate, either by titrating directly against a ferrous solution or adding excess of the same and titrating back with bichromate; potassium ferricyanide is used either as an external indicator or by adding it directly to the solution undergoing titration.

Class C.—Most of the iron is extracted as under Class A, the hydrochloric acid replaced by nitric acid and the vanadium separated from iron, chromium, etc., by pouring into a boiling solution of sodium hydroxide. The vanadium goes into the filtrate, and is precipitated by mercurous or lead salts, the final estimation being either gravimetric or volumetric.

It seems likely that these three classes of methods comprise those most used in this country, inasmuch as the group of coöperating chemists was typical. The same methods are used with little or no change for the analysis of chrome-vanadium steels carrying usually from 0.2–5 per cent. chromium.

SOME SOURCES OF ERROR.

General Errors.—An error in all methods where final titration is made against permanganate may arise by failure to deduct the blank caused by the presence of elements other than vanadium; this may be particularly high in such methods as that of Campagne where, if the ether extraction is not carefully done, there may be large amounts of ferric sulphate present during the titration. Campagne himself² speaks of this point, but it is not usually mentioned in text-books. If salts yielding green or blue solutions are present these may obscure the true end-point, requiring several tenths of a cubic centimeter of tenth-normal permanganate in excess. Indeed, in low vanadium products the blank may be much larger than the amount required by the vanadium, or if the analyst does not make a qualitative test for vanadium he may report its presence when the steel contains none. Another point to be observed is the temperature of the solution being titrated. The optimum temperature is 70–80° C.³ It is almost impossible to secure a good end-point in a cold solution. On the other hand the work of Sarkar and Dutta⁴ and of others on the reduction of permanganate by hot sulphuric acid

¹ *Ber.*, **36**, 3164 (1903).

² *Loc. cit.*

³ Hillebrand, "Analysis of Silicate and Carbonate Rocks," *Bull.* **422**, p. 151, U. S. Geol. Survey.

⁴ *Z. anorg. Chem.*, **67**, 225 (1910).

solutions of manganous sulphate shows the importance of not titrating at too high a temperature.

Errors Incident to Methods of Class A.—(1) During the ether extraction there is almost always some iron reduced to the ferrous condition; this is not always reoxidized during the course of the analysis before the titration and therefore might be calculated as vanadium if this fact is not taken into consideration.

(2) The ether, or impurities in it, may act on the strong sulphuric acid when the solution is evaporated to small volume with this acid. There are then present substances which may act on permanganate. In this laboratory separation of carbonaceous material has been observed at this stage, with accompanying odor of sulphur dioxide.

(3) The addition of sulphuric acid before the solution has been repeatedly evaporated with fresh portions of hydrochloric acid is to be avoided, because, if the sulphuric acid is added before reduction of vanadium to the quadrivalent state has been attained, the reduction is likely to be incomplete.

(4) If the evaporation with strong sulphuric acid is too prolonged or carried out at too high a temperature the reverse reaction, resulting in the oxidation of vanadium tetroxide to vanadium pentoxide by the sulphur trioxide, may take place.¹

(5) No other metals capable of oxidation to higher valence by permanganate should be present. Those most likely to be encountered in steel analysis are chromium, molybdenum, and tungsten. The latter two may be removed before titration without great difficulty; the methods hitherto given for separating vanadium and chromium are so laborious that this precaution is often omitted in the case of chromium. A correction for the latter is invariably necessary, particularly in some steels where the chromium and vanadium may be present in the ratio of twenty or forty to one. Moreover, the amount of chromium oxidized to chromic acid is greater when titration is made at 70–80°, as is imperative for a good vanadium end-point, than where the solution is titrated cold, as is sometimes recommended. For details regarding this correction for chromium see "Analysis of Silicate and Carbonate Rocks."²

Errors Incident to Methods of Class B.—Methods requiring the use of ferricyanide as indicator for ferrous salts, when quadrivalent vanadium and ferrous salts are also present, must of necessity be very uncertain, yet these are the conditions under which the determination is carried out. The reason for this is very evident when it is remembered that ferricyanide in acid solution rapidly oxidizes quadrivalent vanadium to the quinquivalent condition with resulting production of ferrocyanide. The latter reacts at once with the ferric iron, so that a blue color is present in the drops of indicator as soon as an appreciable amount of vanadium is reduced and long before the color due to excess of the titrating solution makes its appearance. Consequently such methods, if at all applicable, must yield results varying with the operator and requiring

arbitrary and uncertain correction factors. Much difficulty was experienced in attempting to determine vanadium in pure vanadium solutions by this method; the reason for this, as stated above, was soon discovered, and later, references to the same matter were found in the literature.¹

Errors Incident to Methods of Class C.—Vanadium is almost always carried down by the precipitate of ferric and chromic hydroxides, etc., upon pouring into sodium hydroxide. Usually two or three precipitations are necessary to obtain all the vanadium in the alkaline filtrate. The difficulty seems to be largely due to the presence of manganese, which of course the ether does not extract, for by working in the absence of manganese it has been found possible to make good separations with one precipitation. However, there is no simple method for removing manganese at this stage of a vanadium determination in steel without introducing other complications. If chromium is present another difficulty is added, for part of the manganese is oxidized by the air and precipitated while the sodium hydroxide solution is being boiled to secure complete precipitation of chromium and complete extraction of vanadium from the precipitated hydroxide; this peroxide rapidly oxidizes some of the chromium to chromate, which goes into the filtrate with the vanadium. If the sodium hydroxide precipitation is repeated, or a third precipitation is necessary, as may happen, a very large amount of chromium goes into the filtrate. In fact, the first operation leaves enough chromium with the vanadium to introduce serious error in determining the latter unless a correction is made; furthermore, the same cause may require appreciable correction to be applied to the chromium. The addition of sulphurous acid to the acid solution of the steel just before it is poured into the alkali, as is recommended sometimes, does not help, for of course it is not effective after the solution is strongly alkaline. Another source of trouble is the organic matter mentioned above as sometimes coming from ether; this causes appreciable amounts of iron and chromium to dissolve in the filtrate with the vanadium. It is evident that all of the sources of difficulty, except the last mentioned, are present in even greater degree when an attempt is made to carry out the caustic soda separation without a preliminary extraction of most of the iron by ether. Thus it will be seen that to separate the vanadium from the iron and to obtain all of it in the filtrate may be, and usually is, a long and complicated operation. When this is accomplished there may be present a large amount of chromium, and this occasions another series of difficulties, for the chromate precipitates with the vanadate, whatever the method of precipitation. The only alternative is to titrate the vanadium in presence of the chromium, making the uncertain corrections above-mentioned, or to make an electrolytic separation as described later.

When attempt is made to extract vanadium from steel by fusion of the oxides obtained by evaporation

¹ Koppel and Behrendt, *Z. anorg. Chem.*, **35**, 156 (1903).

² Hillebrand, *Bull.* **422**, pp. 152–4, U. S. Geol. Survey.

¹ Campagne, *Loc. cit.* Brearley and Ibbotson, "Analysis of Steel Works Materials," p. 89.

and baking a nitric acid solution of the metal, an old method which is now probably little used for this class of material, the same series of difficulties as enumerated under Class C is encountered. It seems almost impracticable to extract quantitatively, say one-tenth of 1 per cent. of vanadium in this manner without undue expenditure of time and labor.

It is clear, then, that there are marked defects in the most commonly used methods for determining vanadium in steel, unless the analysis is conducted with extreme care, requiring more time than is usually available in a technical laboratory, or unless the analyst is so experienced that he can recognize and correct for disturbing factors. Accordingly, the present research was started with the hope that a simpler and more accurate procedure might be outlined, and one which would at the same time be reasonably short.

PRELIMINARY WORK TOWARD A NEW METHOD FOR VANADIUM.

Much work was done with the idea of determining vanadium without a preliminary separation from iron. It seemed possible that the vanadium might be oxidized to vanadate and then reduced by hydrobromic acid by distilling in an apparatus suitable for collecting the liberated bromine in alkali. The difficulty, however, is to secure oxidation of the vanadium and then get rid of the excess of oxidizer without at the same time reducing some vanadic acid. It was found that the vanadium of a dilute sulphuric acid solution of a vanadium or chrome vanadium steel could be oxidized easily enough in the cold by manganese dioxide without converting any noticeable amount of chromium to chromate, the excess of manganese dioxide being eliminated by filtration. But when such a solution was placed in the distilling apparatus and distilled after the addition of a large excess of hydrochloric acid and potassium bromide, as recommended by Edgar,¹ there was almost always more bromine liberated than corresponded to the vanadium present. Many efforts were made to get rid of the disturbance, such as long boiling of the oxidized steel solution before placing in the distilling apparatus, reduction of the amount of sulphuric acid used for solution to the minimum necessary, etc., but while the results were usually as accurate as those obtained by any of the methods above described there were occasional and unexplained irregularities which finally led to the abandonment of the method for technical purposes. This is regrettable, for, theoretically, such a procedure is ideal; practically it would be extremely short and simple. It seems likely that the trouble experienced was due either to the known solubility of manganese dioxide in sulphuric acid or to the action of sulphuric acid itself on the hydrobromic acid in the strongly acidified solution in the distilling flask.

From this it appeared desirable to develop a method which would obtain the vanadium in a solution free from all other metals, so that one might always be certain that the oxidizing or reducing action, which-

ever is made the basis of a volumetric method, exerted by vanadium compounds and nothing else. The manner of accomplishing this was suggested part by a dissertation of Albert Steffan² who used barium carbonate for precipitating vanadium and chromium, together with relatively little iron, from the (ferrous) solution of the steel. The principle, the base of the method has long been applied to other separations. It has invariably been recommended until recently to conduct this precipitation in the cold, shaking frequently and allowing to stand for many hours. It has been found, however, by numerous experiments here that a few minutes' boiling with the carbonate will completely precipitate much larger amounts of vanadium and chromium than are likely to be encountered in steel analysis; furthermore, the precipitates are free from manganese, a distinct advantage, from many standpoints over the ether separation. The shortening of the time required for precipitation when solutions are boiled has recently been noted by others in connection with steel analysis, also the use of zinc oxide as a precipitant.³ The precipitate obtained in this way contains the insoluble matter from the solution of the steel, a little iron, all the chromium and vanadium, and a considerable excess of the precipitant. The vanadium and chromium may be extracted by fusion with sodium carbonate, but the barium holds vanadium tenaciously and more than one fusion is usually necessary, so that the way of handling the precipitate, although apparently simpler, is longer than the one to be described later.

Smith³ describes an electrolytic method for separating vanadium from iron by driving the latter into a mercury cathode, and in another section he gives directions for electrolytically precipitating chromium under practically the same conditions, hence it appeared feasible to separate both iron and chromium from vanadium by electrolysis when the three are together. Preliminary experiment showed this to be possible, and it was then decided to dissolve the precipitate mentioned above in appropriate manner and submit it to electrolysis in order to obtain a pure vanadium solution. It seemed desirable, however, to be rid of the excess of the precipitant before electrolyzing. The necessary excess being relatively large, it would take too long to drive the iron and chromium out of solution if the precipitant were to accompany them into solution and be deposited along with them, as would be the case with zinc oxide, for instance. Moreover, it seemed desirable to dissolve the steel in sulphuric acid, as the electrolytic deposition is made from sulphate solution. This of course made inconvenient the use of barium carbonate as precipitant. It was therefore decided to try the suitability of cadmium carbonate for the purpose, with the idea of throwing out the excess of cadmium by hydrogen sulphide from the acid solution of the carbonate precipitate. This method gave entirely satisfactory results; the rate of precipitation of the

¹ "Ueber die Bestimmung von Kleinen Mengen an Chrom und Vanadium in Gesteinen und Stahlarten," Zurich, 1902.

² Slavik, *Chem.-Ztg.*, **34**, 648 (1910).

³ "Electroanalysis," fourth edition, p. 258.

¹ *Am. Jour. Sci.*, **27**, 174 (1909).

vanadium and chromium seems even more rapid than with zinc oxide or barium carbonate. The precipitate of cadmium sulphide obtained in a boiling, very slightly acid solution is easily filtered and never carries down vanadium.

The precipitation of vanadium and chromium from a reduced and boiling solution of steel by any of the precipitants herein mentioned succeeds equally well in hydrochloric or sulphuric solutions, but seems to proceed a little faster with cadmium carbonate and a sulphate solution.

THE METHOD IN DETAIL.

Dissolve 2-4 grams of steel in 40-60 cc. of 10 per cent. (by volume) sulphuric acid, in a covered 300 cc. Erlenmeyer flask. Filter off the insoluble, wash two or three times with water, ignite and fuse for a few minutes with acid potassium sulphate, adding the aqueous solution of the fusion to the main solution. If the steel will not dissolve readily in sulphuric acid, hydrochloric acid may be used, fusing the insoluble as before.¹ Nearly neutralize the solution of the steel with saturated sodium carbonate solution. Then add finely pulverized cadmium carbonate in small portions at intervals of four or five minutes, boiling vigorously between times, keeping the flask well covered. A gram or two of carbonate should remain undissolved at the end of the operation. About fifteen or twenty minutes' boiling always suffices. The time may be even shorter for vanadium steels containing little or no chromium. Allow the precipitate to settle and filter rapidly, so as to prevent oxidation and precipitation of iron on the filter (an 11 cm. S. and S. No. 589 white label filter is recommended). Wash the precipitate twice with hot water; no care need be taken to remove all of it from the flask. Dissolve the precipitate with the minimum of nearly boiling 10 per cent. sulphuric acid, catching the filtrate in the flask. Boil to insure solution of material adhering to the sides of the flask. Cool and nearly neutralize with ammonia; there should be no more free acid present than is necessary to prevent the iron from precipitating by hydrolysis when the solution is boiled. Pass a rapid current of hydrogen sulphide for a few minutes while the solution is boiling vigorously. Let the precipitate settle, filter it off and wash two or three times with hot water. Concentrate the filtrate if necessary and electrolyze in a volume of 60-70 cc., using 5-6 amperes at 6-7 volts. The amount of mercury used in the special apparatus described below was about 200 grams. The solution is tested for iron by ferricyanide; usually when no iron test is obtained all the chromium is removed. However, should there be an unusually large amount of chromium relatively to the iron this might not happen. In this case the test should be made by removing 3 or 4 cc. of the solution, adding a few drops of hydrogen peroxide and boiling for a few minutes after the brown color, due to vanadium peroxide,

¹ In this case the carbonate precipitate must be dissolved in sulphuric acid and the separation repeated in sulphate solution, for the precipitate first obtained contains enough chloride to give trouble if dissolved in sulphuric acid and directly electrolyzed.

disappears. If the solution is colorless on adding ammonia, the electrolysis is ended. Acidify the test portion with sulphuric acid before returning it to the electrolyzing apparatus. The simpler ferricyanide test usually answers for all purposes; the complications mentioned earlier, due to reduction of ferricyanide by quadrivalent vanadium, do not interfere in this case, inasmuch as there is no ferric iron to react with the resulting ferrocyanide. When the solution no longer gives a test for iron or chromium, remove it from the apparatus and wash the mercury two or three times with 25 or 30 cc. of water while the current is still passing. Add 2 or 3 cc. of sulphuric acid (1:1 by volume), heat to 70° or 80° C. and add permanganate from a pipette until there is a strong pink color. Run sulphur dioxide into the boiling solution for a few minutes; then pass a rapid current of carbon dioxide until the escaping steam gives no test for sulphur dioxide. Filter, preferably through asbestos² or a Munroe crucible, cool the solution to 70° or 80° C. and titrate against *N*/50 potassium permanganate. For extreme accuracy repetition of the reduction and titration is recommended. The reduction may also be made by hydrogen sulphide, if desired.³ With special facilities a determination may be completed in 1½ hours, or less.

NOTES AND PRECAUTIONS.

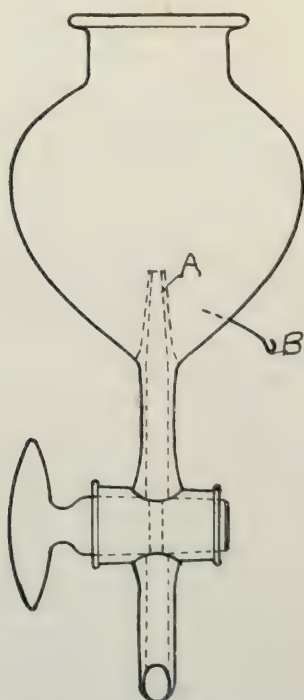
Sufficient exclusion of air is secured by dissolving the steel in a flask kept well covered by a watch-glass. The fusion of the insoluble is absolutely necessary, as a large proportion of vanadium remains here; indeed, Nicolardot has proposed methods whereby, with complete exclusion of air, it is possible to secure practically all the vanadium in the insoluble portion when operating on certain classes of materials. This makes a quick and easy qualitative test for vanadium in steel, for as soon as the carbon is burned off the characteristic appearance of the fused vanadium pentoxide is very striking.

The treatment of the insoluble requires but a few minutes. The operations of solution, of cadmium precipitation and of filtration, must be done promptly, for a delay between solution and precipitation gives opportunity for oxidation of iron. This is to be avoided since it increases the amount of iron going into the carbonate precipitate, thereby prolonging the electrolysis, and also interfering with the complete precipitation of the vanadium and chromium. In this latter connection it seems that the particles of carbonate become rapidly coated with the excessive precipitate of ferric hydroxide, and this interferes with

² The result will be slightly high if a paper filter is used. This is due to the hydrolyzing and solvent action of the acid solution on the paper (even the best washed filter paper). With alkaline solutions very serious errors may be incurred from ignorance of this fact.

³ Bleeker, *Mit. and Chem. Eng.*, 9, 209, April, 1911, reduces vanadate solutions electrolytically, using a platinum dish as cathode. This method appears short and simple and might be adopted in many cases. No work has been done here, however, along this line and the exact conditions for complete reduction to the hypovanadate stage, and no further, would probably have to be determined. It is not safe to titrate directly the solution obtained by electrolyzing as described without the preliminary permanganate oxidation followed by reduction and filtration as above; to do so usually gives irregular results.

their efficiency in neutralizing the solution. The operations of filtering and washing must be particularly rapid; there is no difficulty here if the solution, after boiling, is allowed to stand a few minutes before filtering; the precipitate settles readily and is easily filtered. Two washings with hot water are sufficient. Sometimes a little difficulty is experienced in dissolving the precipitate completely from the filter; this is particularly true if the filtration and washing have not been done rapidly and promptly, giving opportunity for a difficultly soluble coating to form over the surface, due to oxidation and precipitation of iron. However, this trouble will never be serious if the operations are conducted as directed; moreover, even if this iron is not all removed from the filter it is never found to contain vanadium after two or three washings with the dilute acid. The advantage of a carbonate precipitant over an oxide precipitant is shown here, because the carbon dioxide evolved during the process of solution very effectually breaks up the difficultly soluble surface layer, permitting the acid to get at the main body of the precipitate. On the other hand, when using zinc oxide it is often very difficult to dissolve the precipitate with dilute sulphuric acid. The hydrogen sulphide precipitation of the excess of cadmium is accomplished quickly; the solution should be nearly neutralized with ammonia; sodium hydroxide or carbonate should not be used, as in this case sodium would be driven into the mercury during electrolysis, not only prolonging this operation, but introducing other complications; if the degree of acidity is right and a rapid current of



hydrogen sulphide is used, the solution being boiled vigorously while this is passing, the cadmium sulphide settles readily and is easy to filter and wash. The solution after filtration can be transferred at once to the electrolytic apparatus which may have any of the usual forms, such as the convenient small beakers with sealed-in platinum wires at the bottom, described by Smith.¹ If many determinations have to be made, however, the apparatus shown in the figure has been found very convenient.

The apparatus is a separatory funnel, shown in half size in accom-

panying figure with an inwardly projecting tube, A. The bore of the stopcock should preferably be as large as shown. A No. 18 platinum wire is sealed in at B. The apparatus is filled with mercury to within 1 or 2 mm. of the end of tube A, which itself is completely filled with mercury, and electrical connection made to the negative terminal of the battery. The anode may have any of the usual rotating forms. The electrolyzing vessel is conveniently supported by an iron ring clamped to the stand carrying the motor for rotating the anode. When electrolysis is complete the anode is brought as close as possible to the surface of the mercury without short-circuiting, and the electrolyte is allowed to run out by opening the stopcock. The washing is done very easily by a jet of water from a wash-bottle, leaving the stopcock open during the operation, the course of the washing being followed by the ammeter.

If a rotating anode is used the electrolysis is accomplished in 15 or 20 minutes. The mercury may be used over and over again without purification; this is another advantage of removing the excess of precipitant before electrolysis, for the amount of foreign material going into it is thus reduced to a minimum. When a stock of mercury saturated with iron and chromium has accumulated it may be purified by the rapid method of Hildebrand.² A fair degree of purification can be attained in a few minutes by shaking in a separatory funnel with concentrated hydrochloric acid.

ANALYTICAL DATA.

Table I gives some results that have been obtained on synthetic mixtures of chromium, vanadium and iron. The vanadium was added from a stock solution of sodium vanadate which was carefully standardized by reducing several portions with sulphur dioxide and titrating against permanganate; the iron was from a sulphuric acid solution of a Bessemer steel with 0.08 per cent. carbon, and the chromium from a rough standardized chrome-alum solution. Precipitation of cadmium carbonate was made in the presence of 0.1 grams of iron, one-half of the solution of the precipitate being used for electrolyzing.

TABLE I.
Vanadium.

Number.	Present.	Found.	Error.	Chromium
1.....	0.0030	0.0030	0.0000	0.0286
2.....	0.0030	0.0030	0.0000	0.0572
3.....	0.0101	0.0102	+0.0001	0.0358
4.....	0.0117	0.0116	-0.0001	0.0286
5.....	0.0199	0.0204	+0.0005	0.0572
6.....	0.0376	0.0371	-0.0005	0.3150
7.....	0.0407	0.0410	+0.0003	0.3150
8 ²	0.0010	0.0010	0.0000	none

Determinations were made on the vanadium standard of this Bureau, first, from hydrochloric solution; second, from sulphuric solution. Duplicates gave 0.145 per cent. vanadium and 0.142 per cent. vanadium from the hydrochloric solution. To these there had been added 0.0750 gram and 0.1064 gram chromium respectively. In sulphuric solution, there was obtained 0.145 per cent. The mean of several very careful determinations by Bureau chemists, using different methods, was 0.143 per cent. On the new chrome-vanadium standard now in preparation

¹ "Electroanalysis," fourth edition.

² *J. Am. Chem. Soc.*, **31**, 933 (1909).

² In presence of 10 grams of iron.

the method gives 0.203 per cent. and 0.203 per cent. The averaged complete analysis of the vanadium standard and of the chrome-vanadium standard (full data for the latter have not yet been received and the analysis given is not final) are shown below.

TABLE II.

Standard	C	Si	P	S	Mn	V	Cr	Ni	Cu	Mo
Vanadium	0.350	0.303	0.035	0.027	0.669	0.15	0.007	0.009	0.022	0.006
Chrome-vanadium	0.377	0.113	0.043	0.029	0.58	0.197	1.36	0.15	0.056	...

The results show that a satisfactory degree of accuracy is attainable; this may be increased even more, if desired, by using a larger sample of the steel, for there is no reason why the vanadium should not be concentrated from 10 grams or more of steel, if desired. The minimum amount of vanadium here determined equivalent to 0.01 per cent. in a steel (No. 8 of Table I) shows how delicate the method is; the maximum amount (No. 7 of Table I) shows the possibility of using cadmium precipitation, followed by electrolysis, for high vanadium products. The complete and quick precipitation of large amounts of chromium by cadmium carbonate is equally striking; a method for determining chromium in various kinds of steel, based upon these observations, is being worked out in this laboratory.

From what has been said of the effect of the presence of other substances when titrating hypovanadate solutions with permanganate it is evident that a method like this has distinct advantages in eliminating other metals. If the method is to be used for other steels than those for which it was devised, the effect of other metals must be considered. Such metals as copper and nickel would not interfere. The behavior of molybdenum and tungsten in appreciable amounts has not been investigated, but molybdenum, if at all precipitated by cadmium carbonate, may be eliminated during the hydrogen sulphide precipitation of the excess of cadmium. Tungsten might be removed by evaporation of the cadmium precipitate with nitric acid, followed by filtration. After conversion of the nitrate to a sulphate solution electrolysis could follow as above described. Titanium would probably be precipitated by the cadmium and remain with the vanadium through the electrolysis; however, it would not be reduced by sulphur dioxide nor hydrogen sulphide. These points will be investigated as opportunity permits.

SUMMARY.

(1) Various errors in the usual methods for determining vanadium in steel are pointed out and in a few cases methods for correcting or eliminating these are indicated.

(2) A short and accurate method for determining vanadium in vanadium and chrome-vanadium steels is discussed and described.

The writer is indebted to Doctor Hillebrand for many helpful suggestions during the course of this investigation.

BUREAU OF STANDARDS,
WASHINGTON, D. C.

A RECENTLY DISCOVERED BACTERIAL DECOMPOSITION OF SUCROSE.

D. W. F. (1911)
Read before the Louisiana Section, Am. Chem. Soc., Feb. 17, 1911

The knowledge of the association of bacteria with the fermentation of saccharine fluids is most probably as old as the science itself. Although the investigations that led to the discovery of bacteria by Antony Leuwenhoeck, who is known as the father of bacteriology, were most likely actuated by his interest in microscopy rather than biology, yet it is but natural to assume that the study of fermentation must have had a great influence upon bacteriological investigations. Almost a century elapsed after the immortal Leuwenhoeck's discovery of unicellular life before the importance of his achievement was sufficiently realized to direct the attention of other investigators to the subject. It was during the middle of the nineteenth century, at the time when discussions of the nature of fermentation were at the highest point and were interesting the great chemists of that day, when the investigations that paved the way to modern bacteriology were conducted. The wide-spread interest in the subject of fermentation during that period must have given great impetus to the development of the science of agricultural bacteriology, the science which in its comparatively brief period of existence has contributed untold blessings to mankind. It is particularly interesting to trace the influence of the alcoholic industry upon the science of bacteriology, for it shows that as it was various speculations regarding the decomposition of sucrose that gave birth to the science of bacteriology, so this science has in turn been recently applied to explain a new decomposition to which sucrose is susceptible. The evolution of the alcoholic industry, from its infancy in the earliest history of mankind to its present state of scientific perfection, has been intimately associated with notable discoveries in bacteriology. It was in the investigation of various phases of the alcoholic industry that many new discoveries were made of the products of bacterial action. As the manufacture of alcohol became more scientific it was but natural that greater attention was paid to the investigation of various species of bacteria in their relation to fermentation of sugars. As a result of the interest created by the alcoholic industry in the bacterial action upon sugars the various products of this action became widely known and methods were rapidly evolved to prevent the destructive activities of bacteria upon the fermentation of alcohol. The bacteriological investigations of the fermentation of sugars were chiefly concerned, however, with the discovery of the species of bacteria that were particularly inimical to the process of alcoholic fermentation by yeasts, and as soon as methods were discovered to overcome this trouble further investigations were unnecessary and consequently unpopular. At the time when these investigations were regarded as of only indirect interest in the fermentation indus-

try, the investigations of the action of yeasts upon sugars were vigorously conducted.

During this period of investigative activity, the enzyme invertase which causes decomposition of sucrose into dextrose and levulose was isolated from yeast by Berthelot, but a quarter of a century elapsed after this discovery before Buchner successfully isolated zymase, the enzyme causing alcoholic fermentation. As a result of these researches the subject of alcoholic fermentation was well understood in all its various phases, and attention was again directed to the investigation of the bacterial decomposition of sucrose. The action of bacteria on that particular group of sugars which are known as the hexoses having been quite thoroughly investigated, many scientists began to occupy themselves with the study of bacterial action on sucrose. About this time interest in the question of the ability of bacteria to invert sucrose was renewed, and a number of investigations were conducted upon the subject. Prominent among the investigators of the subject are the names of Fermi and Montesano, who after very exhaustive researches concluded that only a very few bacteria had the power of breaking down sucrose into dextrose and levulose through inversion. Thus it will be seen that the investigation of the subject of bacterial action upon sucrose did not result in discovering any appreciable power on the part of these microorganisms to bring about a decomposition of this material. The work of the above-named authors, applying as it did to a great many species of bacteria under a great variety of conditions, did not tend to prove very convincing of the ability of bacteria to induce deterioration of sucrose by this means. Unlike the alcoholic industry, the sugar industry has only in comparatively recent years been sufficiently concerned with the dangers of bacterial fermentation to promote any definite lines of investigation upon this subject. On that account the sugar industry had not until recently been the means of extending our knowledge upon the subject of bacterial action upon sucrose. From time immemorial the sugar manufacturers doubtless realized the danger from bacterial fermentation, but owing to the fact that few of these products are very susceptible to such deteriorative changes of the sort, and as such products are seldom exposed to the action of bacteria for any great length of time, such dangers as have existed have been quite readily overcome. The sugar maker, just as the alcohol manufacturer, is concerned with bacteriology only insofar as it may enable him to prevent the access of these microorganisms into his products; but as the manufacture of alcohol necessitates both longer exposures to bacterial action and working with products very much more readily fermented than in case of the sugar products, the alcohol manufacturers have been compelled to give more attention to the subject. The sugar maker has been accustomed to regard his sugars as products beyond the reach of his microscopic enemies, and when his raw product—the cane juice of the mill—has reached the stage of crystallized sugar it is, as he thinks, no

longer susceptible to bacterial fermentation. It is highly probable, however, that cases of the deterioration of sugars were observed even in the earliest times. It is certainly very reasonable to suppose that bacteria have been developing in sugars for many ages, but it has been so customary to attribute a fall of the polarization of sugars to lack of uniformity in sampling or to other causes of the kind, that not until very recently has the true nature of the deterioration been suspected. Owing to the prevalent opinion, not only on the part of the sugar manufacturer, but also on the part of scientists in general, that sugars are not favorable media for bacterial development the true cause of the deterioration in sugars remained unsuspected for a long time. It is only fair, therefore, to the sugar manufacturer, to say in his behalf and in defense of his scientific knowledge, that he had many inferences of a scientific nature to justify him in his belief that bacteria could not develop in sugar. So prevalent has been this opinion that we have been accustomed to look upon sugar more in the nature of an antiseptic than a product susceptible to bacterial action and so confirmed have we been in this idea that we have in many cases been in the habit of using sugars in the preservation of food products as one might use an antiseptic. Indeed, the preservative properties of sugars have been so widely talked of that we might have had reason to entertain the fear that some of our over-enthusiastic pure food authorities might place that product under the ban of the law and might forbid its use, owing to its supposed preservative properties.

About ten years ago the various theories of the deterioration of sugar developed into exact knowledge of this phenomenon and it was found that bacteria were associated with and found to be the cause of this phenomenon. At a little later period the various organisms found in sugars were isolated and their characteristics thoroughly studied. In the early investigations of the subject the Sugar Experiment Station took a prominent part, and the investigations there conducted were doubtless responsible for much of the research of the kind that followed. The earlier investigations of this subject attracted much attention, and as the great possibilities of this field of investigation were revealed a research of this kind was instituted in various parts of the sugar world. As a result of the early investigations that had been instituted at the station, a Department of Bacteriology was established in 1908 with the view of taking up as a matter of first importance an investigation of the deterioration of raw sugars. Accordingly, investigations of the subject were promptly instituted and the results of the two years' work—of which this paper is a summary—have recently been issued in bulletin form. Every investigation of bacterial action must necessarily take an account of the following factors: (1) The species of microorganisms associated with the action and their various characteristics; (2) the nature of the action and the conditions affecting it. By applying this general plan to our investigations on the deterioration of sugars we began

by making a thorough study of the bacterial flora of many different grades of sugars. These sugars were procured from the most important sugar-producing countries, and as they represented various climatic conditions and manufacture, it was thought that a study of them would afford adequate data as to the occurrences and distribution of the deteriorative type of bacteria. The species isolated were accordingly studied and were found to be, not as we might have supposed new and unusual numbers of the bacterial kingdom, but old species that had been isolated and studied many years ago. They might be considered as old friends in new surroundings, for they belong to that well known group of bacteria known as the potato bacilli, the members of which are the *Bacillus vulgatus*, *Bacillus mesentericus fuscus*, *Bacillus mesentericus ruber*, *Bacillus mesentericus niger*, *Bacillus mesentericus granulatus*, and are characterized by the very high resistance of their spores to heat. In their newly discovered habitat these organisms were found to have lost little of their old characteristics, and if anything seem to have developed even greater resistance to heat. Our experiments upon this property show that organisms seemed even more resistant as isolated from sugars than when they are taken from the soil. It is very probable that the exposures to the various temperatures incident to sugar manufacture have been responsible for their great resistance. It was found that the deteriorative type of organisms which occurred in cane juice were not destroyed by the various temperatures to which the product was subjected and would be found in the sugar as soon as it dropped from the centrifugal. In order to test the resistance of the spores to bacteria at high temperatures we conducted experiments in the laboratory under conditions where the exposures might be regulated with absolute precision. In the table is given the results of this experiment.

RESISTANCE OF SPORES TO HEAT.

Co.H.	Temperature 212° F.				Temperature 230° F.			
	15".	30".	60".	120".	5".	15".	30".	60".
<i>Bac. vulgatus</i>	—	—	+	—	—	—	—	—
<i>Bac. vulgatus</i> (B).....	—	—	—	—	—	—	—	—
<i>Bac. vulgatus</i> (C).....	—	—	—	+	—	+	+	—
<i>Bac. vulgatus</i> (D).....	—	—	—	—	—	—	—	—
<i>Bac. mes. ruber</i>	—	—	—	—	—	—	—	—
<i>Bac. mes. fuscus</i>	—	—	—	—	—	+	+	—
<i>Bac. mes. fuscus</i> (A).....	—	—	+	+	—	+	+	—
<i>Bac. mes. fuscus</i> (B).....	—	—	+	+	—	—	—	—
<i>Bac. mes. niger</i>	—	—	—	—	—	—	—	—
<i>Bac. liodermes</i>	—	—	—	—	—	—	—	—
<i>Bac. mes. granulatus</i>	—	—	—	+	—	—	—	—
<i>Bac. gummosus</i>	—	—	—	+	—	+	+	—
<i>Bac. megatherium</i>	—	—	—	—	—	—	—	—
(A).....	—	—	—	+	—	—	+	—
<i>Bac. sacchari</i>	—	—	—	+	—	—	—	+
<i>Bac. megatherium</i>	—	—	—	—	—	—	—	—
(B).....	—	—	—	—	—	—	—	—

— indicates spores killed.

— indicates spores capable of germination.

These results show that the spores in some cases could vegetate after several hours' exposure to the temperature of 212°. As the deteriorative type of bacteria are very widely distributed in nature and are always to be found around sugar mills, and as we have

seen from their resistance to high temperatures that they will readily survive the temperature reached in sugar manufacture, we need not wonder at the sources from which sugars become contaminated. The species found in sugars occur almost everywhere, so it is very likely that no sugar house will be free from these organisms. In order to actually determine the various avenues of contamination of sugar products and to learn of the bacterial content of these products during their manufacture, we instituted bacteriological control experiments in the sugar house at various periods during the grinding season. From these experiments we found that the deteriorative type of organisms occurred in all of the product, from the juice to the finished sugar, and were to be found on the canes, in the yards, and in the dust of the buildings. We might say that wherever sugar products are exposed to the air that they would be more likely to become contaminated with this type of organism than from any other species known.

In the following tables are given the bacteriological analyses of the various products in the sugar house, and also in the sugar refinery.

AVERAGE OF RESULTS FROM BACTERIOLOGICAL CONTROL ANALYSES IN THE SUGAR HOUSE OF THE EXPERIMENT STATION SEASONS 1909-1910 AND 1910-1911 "RUNS."

Product.	No. of organisms per gram or cc.	Species.	Presence of species of economic importance.
Raw juice.....	280,000	Yeasts, molds, bact.	—
Sulph. juice.....	35,000	Yeasts, molds, bact.	—
Limed juice.....	37,500	Bact. predominating	+
Defecated juice....	750	Sugar group, bact. E	+
Syrup.....	400	Sugar group, bact. E	—
Massecurite.....	450	Sugar group, bact. E	+
Sugars.....	600	Sugar group, bact. E	—
Molasses.....	35,000	Mixt. contam.	—
Wash water.....	25,000	Mixt. contam.	—
Filter press cake....	1,500,000	Mixt. contam.	+

BACTERIOLOGICAL ANALYSIS OF SAMPLES FROM A REFINERY

Name of sample	Dilution employed	No. of organisms per gram or cc.	Presence of species of economic importance
Raw sugar.....	1 : 100	1,000	+
Raw washings.....	1 : 1000	5,000	—
Washed sugar.....	1 : 100	2,000	+
Melted washed sugar.....	1 : 100	800	—
Def. wash sugar and liquor.....	1 : 200	800	+
Bag filt. wash sugar and liquor.....	1 : 1000	3,000	Moulds and bacteria
Light sweet water.....	1 : 1000	1,000	—
Clear filtered liquor.....	1 : 1000	6,000	—
Defecated washings.....	1 : 1000	5,000	+
Bag filtered washings.....	1 : 1000	8,000	+
Dark sweet waters.....	1 : 2000	8,000	+
Char filt. washings.....	1 : 400	8,000	+
Mud water.....	1 : 2000	400,000	—
Press cake.....	1 : 2000	No development	—
Press water.....	1 : 1000	20,000	+
Cone sweet water.....	1 : 1000	300	+
Granulated magma.....	1 : 100	5,000	—
Granulated syrup.....	1 : 1000	150	—
Wet granulated sugar.....	1 : 50	150	—
Dry granulated sugar.....	1 : 50	200	+
Remelted magma.....	1 : 50	25,000	—
Remelted syrup.....	1 : 1000	10,000	—
Undefecated liquor.....	1 : 500	500	—
Remelted sugar.....	1 : 500	3,000	—
Car sugar.....	1 : 100	8,000	—
Barrel syrup.....	1 : 100	400	—
Car syrup, two weeks in hot room.....	1 : 100	400	—

It is interesting to note that on an average of ten runs in the Experiment Station sugar house, there was a decrease of approximately 87 per cent. of the organisms occurring in the sulphured juice over the number of organisms occurring in the raw juice. This is very likely to be attributed to the precipitation of the sulphitation process rather than to the germicidal action of the sulphurous acid. After investigating the bacterial flora of sugars quite thoroughly and learning of their various characteristics, it was next necessary to investigate the nature of this action upon sucrose. We endeavored, therefore, to determine the exact means by which these organisms caused decomposition of sucrose. Was the deterioration of sucrose due to an invertase action exercised by the bacteria, or was it new decomposition? As the decomposition of sucrose into dextrose and levulose by the enzyme invertase was the only decomposition to which this substance was known to be susceptible by microorganisms, it was but natural for investigators of the subject to attribute the deterioration of sugars to this action. Such a theory of the nature of the deterioration of sugars is not exactly in accord with what has been found to be true as to the condition governing inversion by invertase. In the first place, the concentration of sucrose in the film of moisture, surrounding the crystals of sugar, is too high to be favorable for such action, and in addition to this, unfavorable conditions of concentration bacteria, as we have previously observed, have never been known to be very active in causing inversion of sucrose. In the premises of the case, therefore, it would seem that the deterioration of sugars by bacteria must be due to some other action upon sucrose, and if this action is not due to the secretion of invertase, how shall we explain it? For evidently we have no precedent in the subject to which to attribute it.

A few years ago an investigator of this subject discovered that bacteria isolated from sugar had the power of inducing what he termed gum fermentation of sucrose solution. This author isolated the gum thus formed and gave it the name of *Levan* on account of its levorotary nature. This investigator was Greig Smith, a bacteriologist in New South Wales, and his work attracted considerable attention at that time. According to this author the origin of this gum was sucrose, but this substance had to be transformed by the inverting action of the bacteria into dextrose and levulose before it could be converted into levan. It seems never to have occurred to him that levan was formed to any extent by these organisms in raw sugars, so he was very probably under the impression that the deterioration of sugars was due to the inverting action of the organisms rather than the gum-forming action, which he himself had discovered in sugar solution. Smith very likely supposed that the action of the bacteria upon sucrose in raw sugars were confined to inverting the sucrose, while in sugar solution their action extended to the gum fermentation of the invert sugars thus formed. It will be quite unlikely, it seems, for the

same bacteria to exercise a different action upon raw sugars from that which had been found to take place in solution. Our experiments in determining the rate of deterioration of sugars under the natural conditions and under conditions of artificial inoculation yielded certain results which indicated that certain bodies must have been formed which introduced an error in our analytical work. In many cases we found, to our surprise and great astonishment, that our Clerget analyses on sugars showed an increase rather than a decrease of sucrose. From many of these analyses it appeared that sugars, not unlike whiskey, tend to improve on storage. As measured by the single polarization, the sugars were deteriorating very rapidly. To what then was this discrepancy between single polarization and the Clerget method due? These results were too constant to attribute them to any incidental error in manipulation. We soon found this to be the rule rather than the exception in our sugar analyses. The formula for determining sucrose by the Clerget method of analysis is based upon the fact that in the inversion by hydrochloric acid none of the optically active bodies present other than sucrose shall have their respective readings increased or decreased in the process. The reliability of the method depends, as you all know, upon the fulfilment of these conditions. Any body, therefore, that may be present in the sugar and which would have its optical activity either increased or decreased or changed in regard to its original direction of rotation by the hydrochloric acid inversion would necessarily introduce an error in the analysis. So it was that the increase in our Clerget analysis over the single polarization suggested to us the fact that some optically active body had been formed in the sugars that we were investigating. As the organisms found in sugars have been found to possess the power of forming gum levan from sucrose, it was the formation of this gum that was suspected to be responsible for the increase in sucrose as determined by the Clerget method of analysis. Levan having an optical activity of about 40 becomes hydrolyzed through the inversion with hydrochloric acid, and the levulose has an optical activity of about 89.2. This increase in optical activity will very readily account for the error in the analytical determination. In order to overcome this difficulty we endeavored to devise some method of bringing about the inversion for invert reading by some other means than ordinary hydrochloric acid methods. In certain cases the use of prepared invertase has been recommended for this inversion and it was thought that if this substance was found to have no action on levan it could be used with very satisfactory results. It has been our experience, however, in using invertase that so much care is necessary in order to attain the exact point of acidity necessary for the complete inversion of the substance that it is impracticable to use this method to any great extent.

Mr. W. G. Taggart, of the Sugar Experiment Station, who as the assistant chemist has been in charge of the analytical work of this department, has prepared

considerable data on the influence of levan on the analysis of sugar, as well as the results of his experiments with the invertase method of sucrose determination. I feel quite certain that he will be only too glad to give you the facts of his experiments should you desire them.

As an example of the influence of levan on the analysis of sugars, we give the following results from the analyses of sugar samples:

	Single polariza- tion.	Sucrose (Clerget.)	True sucrose invertase method.
Sample No. 1, refined sugar.	99.98	99.99	99.98
Sample No. II, Inoculated so- lution containing gum.	0.00	0.8	0.17
Sample No. III, Peruvian crystals.	91.20	95.0	91.4
Sample No. IV, from Gram- ercy.	87.0	89.82	87.6

It is interesting to note the difference in sucrose (Clerget), and the single polarization. In the analyses of solutions containing 10 per cent. of sucrose which were undergoing a gum fermentation by the micro-organism investigated, a comparison between the single polarization and the Clerget and the true sucrose (corrected Clerget) are as follows:

EXPERIMENT NO. VII.—GUM DEVELOPMENT AS AFFECTED BY DURATION OF INOCULATION PERIOD. CULTURE USED, *BACILLUS VULGATUS*.

Age of cult. Days.	Acidity 25 grams Cc. N/10.	Reducing sugar.	Single polariza- tion.	Clerget.	True sucrose (corrected Clerget).	Gum.
..	9.2
2	2.50	2.33	5.6	6.74	6.04	1.05
4	2.80	5.56	2.0	4.83	3.65	1.77
6	6.78	0.0	2.30	0.11	3.28
8	2.80	7.28	-0.4	2.30	0.76	2.82
10	2.6	6.90	-0.4	1.63	2.59
13	2.6	6.90	-1.3	1.85
15	2.3	7.14	-1.2	1.35	1.98
17	2.2	7.14	-1.3	2.36
20	2.4	7.14	-1.3	1.66	1.34
22	2.1	7.14	-1.8	1.25	1.88
28	3.0	7.84	-1.8	1.16	(2.37)
34	3.2	7.28	-2.1	1.00	1.69
42	3.6	7.84	-2.2	0.26	0.65

From this table it will be noted that all the sucrose was really destroyed by the eighth day, as shown by the corrected Clerget, while by the ordinary Clerget method the sucrose readings were obtained as long as 42 days. The true sucrose was computed by correcting the Clerget analysis upon the basis of the influence of the amount of gum formed in the solution. Although convinced by the great amount of evidence that was at hand that levan was present in the sugars and that it was responsible for the analytical errors, we could not succeed in separating it in such a state of purity as would permit of its identification in those sugars where it was strongly suspected. Precipitation with alcohol brought down so many impurities that it was impossible to separate the gum to a point where it could be definitely identified. We were often successful to the point of obtaining levorotary precipitates, but the other properties of levan were lost. In order to prove, however, that our failure to isolate levan from the sugars in which we suspected it was not proof of its absence, we

sometimes added small quantities of the gum to these sugars and failed to recover it by alcoholic precipitation. It seems evident that gum formation takes place in sugars, and it is this means by which the organisms occurring therein cause decomposition of the sugars. We have already noted the fact that the conditions obtaining in sugars are not all suitable for the action of invertase. It was found that the formation of levan could take place only where there was sucrose present. Invertase has been found to be most active in an acid solution and entirely inactive under alkaline conditions. Just the reverse we have found to be true of the formation of levan, which seems far more energetic in a slightly alkaline solution. We were not able to produce it from dextrose and levulose or from a mixture of these two sugars, and as we have found the presence of sucrose to be essential to the formation of gum, and as its decomposition into gum is most active under conditions known to be unfavorable for inversion into dextrose and levulose, it seems evident that micro-organisms must have the power of decomposing sucrose into gum and reducing sugar direct. Since reducing sugars are always found to develop concurrently with levan in this fermentation of sucrose, we must conclude that these two substances are both formed in the fermentation. This newly discovered decomposition takes place according to the following reaction:



Greig Smith, the bacteriologist, who made quite an investigation of the gum fermentation of sucrose, advances the theory that levan was formed from sucrose indirectly. He claimed that the organism first inverted sucrose and from the nascent dextrose and levulose thus formed the organism produced the gum levan. This author very probably arrived at this conclusion because he found the organism was not able to produce the gum in those sugars in their natural condition. He naturally concluded therefore that those sugars possessed some quality when in the nascent stages that made them favorable for the gum fermentation. In order to disprove this theory of the formation of levan from nascent dextrose and levulose, we conducted experiments upon sugar solution inoculated with both gum-forming bacteria together with yeast. In these experiments we found that the formation of gum where bacteria were used alone was much greater than where both yeast and bacteria were used together. If nascent levulose and dextrose were the origin of the gum we should have expected much greater gum formation to have taken place where the yeasts and bacteria were used. As yeasts have greater inverting power than bacteria, there should have been more invert sugar formed in that condition than where bacteria are used alone. A microscopical examination of the solution showed an abundance of yeast cells and bacteria in the solution in a flask which was inoculated with both classes of micro-organisms. A chemical analysis also showed that much more reducing sugars had been formed where the yeasts were used, so that if the Smith theory

was right, conditions were certainly more favorable for gum formation than where the bacteria were used alone. But, as a matter of fact, there was almost twice as much gum formed in a flask containing the bacteria as in the one in which yeasts also were used. It appeared evident that the sucrose inverted by the yeasts was no longer favorable for gum formation. These results indicate very strongly that nascent levulose and dextrose were not the origin of the gum. In consideration of the facts therefore that gum formation takes place only where sucrose is present, and as this action seems to be accelerated in conditions of concentration of medium and alkalinity of the solution known to be unfavorable to invertase, it seems evident that we are here dealing with an absolutely new decomposition of sucrose. This belief is further strengthened by the fact that bacteria have never been found to invert sucrose to any great extent, and that the nascent products of inversion seem to be no more favorable to gum formation than dextrose and levulose in their natural state. We have succeeded in isolating the enzyme causing the decomposition of sucrose by growing cultures of the *Bacillus vulgatus* on agar agar in large moist chambers and taking the surface growth after about ten days old, we found that we could use this growth after the bacteria had been killed by an antiseptic with the same results as from the living cultures. The large mass of growth was usually spread upon the surface of a plate and ground up with powder glass. This pulverized mass was then dissolved in water and precipitated with alcohol. By this method we obtained a dark powder which, when introduced into a sugar solution containing sufficient toluene to prevent bacterial growth, induced an active gum formation just as when the living cells of bacteria are used. In these experiments a microscopical examination shows that there were no living cells developing in the solution, so that any changes that had taken place must have been due to an enzyme. It was, however, found in experimenting with this bacterial extract that gums and reducing sugars were formed, which is further proof of the correctness of our theory as to the decomposition of sucrose in the gum and reducing sugars. For this new enzyme we have proposed the name *levanase*, and are now engaged in investigating its properties in the laboratories of the experiment station.

In conclusion, I would say to the members of this scientific society that the facts presented in this paper should naturally direct your attention to means of obtaining more reliable methods than are now available for the determination of sucrose. The investigation herein reported is convincing of the fact that practically all of our unrefined sugars are contaminated with the sucrose-decomposing bacteria. On this account the sucrose is continually subject to this action which might readily account for the many litigations regarding discrepancies in analyses that are so current at this time. Were the deterioration of sugars due to the breaking down of sucrose into dextrose and levulose, as is the case in direct inversion,

we would have no reason to concern ourselves with the elaboration of new methods, for in that case our present Clerget would suffice. But in the light of this discovery of the transformation of sucrose into reducing sugars and an optically active gum, which is very likely of a transitory nature, we must agree that under such conditions our present methods of sucrose determination are very unreliable and ought to be improved upon.

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EXTRACTION OF GRAINS AND CATTLE FOODS FOR THE DETERMINATION OF SUGARS: A COMPARISON OF THE ALCOHOL AND THE SODIUM CARBONATE DIGESTIONS.

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INTRODUCTION.

There has been some discussion among chemists as to methods of determining sugars in agricultural products, such as grains, plants, both dried and fresh, and cattle foods. Figures obtained by different chemists on the same sample varied many times by 1 per cent. or more. This wide variation in results was also noted when the same chemist used different methods or made a slight modification of his own in a printed method. The difficulty experienced was not so much in the actual determination of the sugar as in the solvent and the method of procedure used to obtain an extract on which to work. Again, sometimes the results obtained on one day could not be duplicated on the same sample at a later date. Often this may be attributed to lack of homogeneity of the sample, a fault remedied by better preparation of the material, especially by finer grinding. But the chief difficulty appears to lie in the changes due to enzymic action during or after extraction and also somewhat to the solvent and the clarification agents used. In this class of material, sugars are usually present in small quantities and the other carbohydrates, such as starch, pentosans, gums, etc., in much larger amounts. It is because of the latter substances that the usual water methods for sugar-beet analysis can not be successfully used.

LITERATURE ON THE SUBJECT.

The literature contains but few definite methods for the determination of sugars in grains, although alcohol is often spoken of as the solvent used for extracting materials, especially when sugars are to be obtained. Other references are found to the determination of sugars in the water extract of the material. In the early methods¹ of the Association of Official Agricultural Chemists, the procedure was to "stir 3 grams of the sample in a beaker with 50 cc. of water for an hour," filter, and make up to volume. This procedure gave varying results, depending upon the temperature of the water during extraction and the fineness of the material. Later this procedure was modified by using ice water for extraction and submerging the beaker during extraction into a bath

¹ U. S. Dept. Agr., Bureau of Chemistry, Bull. 46, 24.

of broken ice.¹ In a majority of cases this does not wholly accomplish its purpose, namely, to stop enzymic action and thereby insure concordant results. It is a rather cumbersome procedure, and while enzymes may be inhibited during extraction, they become active again when the filtration is carried on at room temperature. However, many now use this method of procedure for preparing the extract for sugar determination. The official methods offer as an alternate for the water method an extraction with 40 or 50 per cent. alcohol, but no definite procedure is outlined.

O'Sullivan, as early as 1886, was using alcohol to extract barley for the determination of the quantity and kind of sugars present. He states this to be the usual method of determining sugars at that time. Stone,² in 1897, published a method for "The Quantitative Determination of Carbohydrates in Food-stuffs," in which he extracted successively with boiling alcohol, cold water, diastase or malt infusion, dilute hydrochloric acid, and finally 1.25 per cent. sodium hydroxid. The alcohol treatment was for the removal of the true sugars, the cold water for the removal of dextrin and soluble forms of starch. Browne³ published results obtained on a distillery waste by this method, but beyond this little mention of it could be found.

M. N. Straughn, when working with C. G. Church on the sugar content of dried sweet corn at the Maryland Experiment Station in 1902, tried many modifications of the water extraction and alcohol extraction methods. In this product sugars were present in small quantities together with a large percentage of starch, and the enzymes were active, as the drying had been carried on at a low temperature. On extracting this material with cold water great difficulties were experienced in obtaining clear extracts and a rapid filtration. It was soon found that the percentage of total sugars obtained by this method increased with the length of time of extraction, or, if the time of extraction was fixed, the results varied with the time consumed in filtering. This increase was no doubt due to enzymic action. Extraction with hot water could not be practiced, as the material gelatinized, some becoming soluble, and filtration was almost impossible.

Alcoholic digestion was then tried. By this method duplicate results were obtained on different days, and there was an agreement of results whether cold or hot solvents were used, although with cold extraction great difficulty was experienced at times in filtering, but even under these circumstances the results of the sugar determination in the extract, provided evaporation was guarded against, were practically the same. In a study made on the "Influence of Environment on the Composition of Sweet Corn,"⁴ the alcohol digestion method was used.

The sugar laboratory in 1905 conducted a long series of experiments on the various methods of extraction and the solvents to be used for dissolving the

sugars from grain. The results confirmed those of Church and Straughn on the whole. It was found that 50 per cent. alcohol was the best solvent and that the extraction should be carried on hot. At this strength it was noted that all enzymic action seemed to be stopped and the extracts were easily filtered. The method was tried on many dried plants, grains, and numerous other materials sent to this laboratory for examination. Slight modifications have been made in the procedure of the method from time to time, and its final statement is given in the following section.

STATEMENT OF ALCOHOL DIGESTION METHOD.

Place 12 grams of material in a 300 cc. graduated flask,¹ add 150 cc. of 50 per cent. alcohol by volume (carefully neutralized), mix thoroughly, and boil on a steam bath for one hour, using a small funnel in the neck of the flask to condense the vapor. Then cool. If desired, allow it to stand over night. Make up to volume with 95 per cent. alcohol (neutral in reaction), mix thoroughly, allow to settle, transfer 200 cc. to a beaker with a pipette, and evaporate on a steam bath to a volume of from 20-30 cc. The presence of a trace of alcohol is not harmful. Do *not* evaporate the solution to dryness. (By evaporating the 200 cc. portion in a short-necked, balloon-shaped distilling flask, connected with a condenser, 75-80 per cent. of alcohol can be recovered before the material in the flask foams violently. The short neck—1 inch—of these flasks makes it possible to remove the residue easily. The 100 cc. remaining in the digestion flask may be strained through a cotton bag and the alcohol recovered from the liquid as just described. This is easily accomplished and results in a marked saving when a large number of samples are run.) Transfer the contents of the beaker or flask, as the case may be, to a 100 cc. graduated flask, washing thoroughly with water. Add enough of a saturated solution of neutral lead acetate to produce a flocculent precipitate, and allow to stand 15 minutes. At this point the solution may safely stand over night if desired. Make up to the mark with distilled water and pass through a folded filter, carefully saving all of the filtrate, to which add enough anhydrous sodium carbonate to precipitate all the lead, allow to stand 15 minutes, and pour onto an ashless filter. Over 75 cc. of filtrate should be obtained. Test the filtrate for lead with a small quantity of dry sodium carbonate, and if any precipitation occurs add more anhydrous sodium carbonate and re-filter. Use 25 cc. of this clear filtrate together with 25 cc. of water for the determination of reducing sugars by the method of Munson and Walker.² In a 100 cc. graduated flask, place 50 cc. of the same filtrate, add a small piece of litmus paper, and neutralize with acetic acid; then add 5 cc. of concentrated hydrochloric acid, and let stand over night for inversion. (Standing 48 hours does not apparently affect the results.) Then pour the inverted solution into a 400 cc. beaker and neutralize with anhydrous sodium car-

¹ If the material is acid in reaction, it would be well to add from 1-3 grams of precipitated calcium carbonate to neutralize the acidity.

² U. S. Dept. Agr., Bureau of Chemistry, Bull. 107 (revised), 241.

¹ U. S. Dept. of Agr., Bureau of Chemistry, Bull. 107 (revised), 57.

² J. Am. Chem. Soc., 29, 183 (1897).

³ *Ibid.*, 23, 229 (1901).

⁴ U. S. Dept. Agr., Bureau of Chemistry, Bull. 127.

bonate; return it to the 100 cc. flask and make up to the mark. Filter, if necessary, and use 50 cc. for the determination of total sugars as invert by the method of Munson and Walker.¹

The amount of cuprous oxid or copper obtained (see page 489) in either the reducing or the total sugar determination represents the sugar contained in 2 grams of the material. Therefore the weights of the invert sugar divided by 2 and multiplied by 100 give the respective per cents. of sugar as invert. Subtract the per cent. of reducing sugars before inversion from the per cent. of total sugar after inversion, both calculated as invert, and the difference multiplied by 0.95 gives the per cent. of sucrose (see page 491 for expression of results). Since the insoluble material of the grain or cattle food occupies some space in the flask as originally made up, it is necessary to correct for this volume. Results of a large number of determinations on various materials have shown the average volume of 12 grams of material to be 9 cc.; therefore the correction factor for 12 grams in 300 cc. is 0.97, and the percentage figures for reducing sugar and sucrose are to be multiplied by this factor to obtain the true amounts.

STATEMENT OF SODIUM CARBONATE DIGESTION METHOD.

Lately the cold-water extraction method has been improved. Realizing that the trouble experienced with this method of extraction was largely due to the activity of enzymes, it was suggested that a small percentage of sodium carbonate be added to the water used for extraction to inhibit their action.² Based upon this suggestion, a method was devised which in the case of certain grains gave figures which checked with those obtained by the alcohol digestion. The procedure is as follows:

Place 8 grams³ of the finely ground grain in a 250 cc. flask and add 190 cc. of a 0.2 per cent. solution of sodium carbonate. Allow to stand at room temperature for two and one-half hours, shaking intermittently. At the expiration of the time add 10 cc. of a hot saturated potassium alum solution; shake and filter. Use 25 cc. of the solution, the equivalent of 1 gram of material, for reduction by Allihn's method,⁴ calculating the cuprous oxid obtained (see page 489) to dextrose by Allihn's table. To 50 cc. of the solution in a 50-55 cc. flask, add 5 cc. of concentrated hydrochloric acid and allow to stand over night for inversion. Then neutralize the whole solution with sodium carbonate, make up to 100 cc., and in 25 cc. of this (equivalent to half a gram of material) again determine the total reducing sugar by Allihn's method. Sucrose (see page 491) is obtained by multiplying the percentages of dextrose before and after inversion by the factor 1.044,⁵ then subtracting and multiplying

the figure thus obtained by 0.95. No correction of the percentages obtained is necessary for the volume of the material, but when working with very wet material the results should be corrected for the dilution caused by the moisture content of the sample.

COMPARISON OF THE TWO METHODS.

The sodium carbonate digestion method having given good results on grains, the authors decided to test it in comparison with the alcohol method on various classes of material and to determine its limitations or the chance of error from differences in procedure. A number of representative samples were selected and comparative determinations made. The results obtained on samples of corn, wheat, and milo are given in the following table. The results in this table as in all tables are calculated to invert sugar.

RESULTS ON FEEDING STUFFS BY BOTH METHODS.

Serial No.	Substance.	Alcohol digestion method.		Sodium carbonate digestion method.	
		Reducing sugars. Per cent.	Total sugars. Per cent.	Reducing sugars. Per cent.	Total sugars. Per cent.
7893	Corn.....	0.07	1.75	0.21	1.89
7917	Wheat.....	0.07	2.35	0.20	3.00
7916	Milo.....	0.15	1.38	0.25	1.43

These figures show that the two methods give results that are fairly comparable. In the case of the wheat, however, the sodium carbonate method gave results for total sugars that are a little higher than those obtained by the alcohol method. This, no doubt, is due to the fact that trouble was experienced in filtering the extract quickly and clearly after adding the alum, hence allowing the enzymes to become active again, a point which will be considered later in the discussion.

Samples of mixed cattle foods were then examined by the two methods, with the following results:

EXAMINATION OF MIXED CATTLE FOODS BY THE TWO METHODS.

Serial No.	Substance.	Alcohol digestion method.		Sodium carbonate digestion method.	
		Reducing sugars. Per cent.	Total sugars. Per cent.	Reducing sugars. Per cent.	Total sugars. Per cent.
7856-A	Corn, cottonseed-meal, and alfalfa.....	0.00	2.99	0.42	3.30
7935	Corn, alfalfa ¹	0.09	0.26	0.43	0.26

It is to be noted that the sodium carbonate digestion method gives a perceptible quantity of reducing sugars, determined from the weight of the precipitated cuprous oxid. On examination of the cuprous oxid precipitate obtained in the sodium carbonate digestion method it was found that considerable organic matter was occluded in the precipitate, and also some mineral matter. This was traced back to the alum clarification, as alum does not clarify as completely as lead acetate. Using neutral lead acetate instead of alum for clarification in a second set of determinations on this material, the reducing sugar of the first sample came down to 0.00 and of the second sample to

¹ This sample had undergone fermentation.

¹ U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 1071 (revised), 241.

² *This Journal*, 1, 299 (1909).

³ Where only total sugars after inversion are to be determined and the quantity of total sugars is small 8.8 grams are used and extracted in the usual way. Fifty cc. of the solution and 5 cc. of acid are inverted over night. The 55 cc. are neutralized with dry sodium carbonate and 25 cc. used for reduction. The figures obtained for dextrose represent the amount from 1 gram of material.

⁴ U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 107 (revised), 49.

⁵ *Ibid.*, *Bull.* 107 (revised), 58.

0.08 per cent. With the lead clarification it is seen that the results compare more closely.

With other materials, such as molasses feeds and plants, high in nitrogenous bodies, when alum was used as a clarifying agent, it was noted that the precipitated cuprous oxid in the direct reducing-sugar determination was badly contaminated, a greenish flocculent mass occurring quite often. When neutral lead acetate was used no indication of this greenish precipitate was noted in the determination of reducing sugars in these samples. This shows alum to be a poor clarifying agent for sugar determinations by this method and indicates that neutral lead acetate should be used for this purpose. In no case, however, should lead subacetate be used as a clarifying agent, as its power of precipitating reducing sugars is well known.¹

As has been suggested, errors are likely to be introduced in the cuprous oxid weighing method by the presence of mineral salts and organic matter. Fehling's solution being strongly alkaline will cause in some cases a precipitation of salts on the introduction of the sugar solution. For this reason it is better to determine the copper in the precipitated cuprous oxid by some such method as Low's.² Burning the cuprous oxid to cupric oxid will only correct for the organic matter, so it could not replace an actual copper determination.

A comparison of these methods on samples of commercial feeding-stuffs, of which molasses was one of the ingredients, resulted as follows:

RESULTS ON MOLASSES FEEDS BY THE TWO METHODS.

Serial No.	Alcohol digestion method.		Sodium carbonate digestion method.					
	Reducing sugars. Total sugars.		Lead acetate.		Alum clarification.			
			Reducing sugars.	Total sugars.	Reducing sugars.	Total sugars.	Reducing sugars.	Total sugars.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
7894	3.55	7.90	4.54	8.68	5.98	9.07		
7901	4.98	9.86	5.53	10.44	6.15	11.17		
7900	2.54	28.82	3.25	32.15	3.41	32.37		
7934	5.38	10.09	7.11	11.37	(3)	(3)		
8049	1.81	33.65	1.88	34.36	(3)	(3)		
8050	1.15	11.54	1.26	11.89	(3)	(3)		

These figures show some peculiar variations. In the sodium carbonate digestion method when lead was used as the clarifying agent the results are lower and more closely approach the alcohol digestion figures. In samples No. 8049 and 8050 the results by the two methods are fairly comparable, but in the others, and especially in No. 7900, the sodium carbonate digestion method gives much higher figures for the percentage of total sugars, while in Nos. 7894, 7901, and 7934 the increase in total sugars is not so large as the increase in reducing sugars. The original samples left were not large enough to determine the cause of this increase. For sample No. 7900 the increase in total sugars amounts to 3.33 per cent. The results on this sample were carefully checked and the determination was also made by the section of plant physiological chemistry and the results as shown in the table agreed

with those obtained by the sugar laboratory. A portion of the sample was placed in a Soxhlet extractor and extracted with alcohol until no sugar was found in the alcohol by the α -naphthol test. Another portion of the sample was boiled for two and a half hours with a measured quantity of water and the sugar determined in this extract. Little or no starch was present in this sample, so that this method could be used. The results of this work are given in the following table:

CHECK ANALYSES OF SAMPLE No. 7900 MOLASSES FEED, USING SEVERAL METHODS.

Methods	Reducing sugars. Per cent.	Total sugars. Per cent.
Alcohol digestion method ¹	2.54	28.82
Alcohol digestion method ²	2.81	28.98
Alcohol digestion method ³	3.10	29.54
Alcohol extraction (Soxhlet extractor) ⁴	2.75	29.24
Sodium carbonate digestion method ¹	3.41	32.36
Sodium carbonate digestion method ²	3.52	31.74
Sodium carbonate digestion method ³	3.28	32.11
Hot water digestion ³		32.44
Hot water digestion ²	2.94	31.68

The results obtained with alcohol, either by digestion or by extraction, agree among themselves, as do also the results with hot water and cold sodium carbonate digestion, but comparing the figures obtained when water was the extracting agent with those obtained when alcohol was used, there is noted an increase of over 3 per cent. in total sugars extracted by water. Unfortunately after this work was done none of the sample was left on which to study the cause of this difference. It might result (1) because the alcohol did not extract all the sugars; (2) because the sodium carbonate did not inhibit the action of the enzymes; (3) because the cuprous oxid was badly contaminated in the sodium carbonate digestion; (4) because the sodium carbonate method extracts substances which reduce Fehling's solution, especially on inversion, and that are not extracted by alcohol.

The first suggestion is answered by the fact that extraction in a Soxhlet extractor was run to a point at which no reaction for sugar with α -naphthol was given, and the results of this method were practically the same as those obtained by the alcohol digestion method. Also in experiments using 12 grams of sucrose as the material for extraction by the alcohol method in one test and 12 grams of invert sugar in another, there was no sugar remaining undissolved and no sugar was precipitated by the addition of 95 per cent. alcohol to the 300 cc. mark. This shows that the percentage of sucrose and invert sugar up to 100 per cent. would be soluble in the alcohol treatment. The second explanation was shown to be unsatisfactory by extracting the material with boiling water; the results obtained were practically the same as by the sodium carbonate extraction method in the cold and, therefore, the activity of enzymes could not have caused the difference.

¹ Results by Mr. Given.

² Results by Mr. Straughn.

³ Results by Mr. Jacobs.

⁴ Results by Mr. Bryan.

¹ Intern. Sugar Journal, 10, 602 (1908).

² U. S. Dept. Agr., Bureau of Chemistry, Bull. 107 (revised), 241.

³ No results by this method.

The third proposition is refuted by treating the crucibles coming from some of these determinations with nitric acid and determining the copper by Low's method.¹ Calculating this copper to invert sugar, the results were somewhat lower, but practically the same difference remained between the results by the two methods. Having eliminated the other possibilities the cause of the difficulty seems to narrow down to the nature of the substances extracted by the two solvents. Water removes from vegetable matter together with sugars many other substances, such as gums, pentosans, and some glucosids. These as a rule are more soluble in water than in 50 per cent. alcohol and some are rather easily hydrolyzed by acids, yielding reducing sugars. From the previous table it is seen that the principal increase occurs in the total sugars or in the sugars after inversion, and not so much so in the sugars before inversion. A new sample of this particular molasses feed (No. 8049, page 489) was obtained from the manufacturer with a view to studying this point further, but the results on this sample showed such slight differences by the two methods that no further work was deemed necessary. In the case of molasses feeds it is of extreme importance to have the sample finely ground before extraction. Especially is this so when using the alcohol digestion method, as the alcohol tends to hold back gummy material and this might coat the larger particles of the sample and keep them from being extracted. Molasses feeds are difficult to grind at the best, as they cake very readily, but by first drying carefully they can be finely ground.

Having compared the results obtained by the two methods on representative samples, it now remains to study the limitations of these methods.

LIMITATIONS OF THE METHODS.

Sodium Carbonate Digestion Method.

The purpose of the addition of sodium carbonate is to inhibit enzymes. Should the material under extraction be acid in reaction, then a portion or all of the sodium carbonate will be neutralized, and the necessary amount of sodium carbonate to inhibit enzymes will not be present. It was found that the acidity of one sample of molasses food neutralized about 90 per cent. of the sodium carbonate and in two others over 50 per cent. was neutralized. Therefore in using this method it is seen that the acidity of the material must be determined and corrected by the addition of more sodium carbonate, otherwise the results obtained would not be correct if the material contained active enzymes.

As the addition of alum or lead for clarification neutralizes the sodium carbonate, and therefore removes the agent inhibiting enzymic action, the procedure from this point must be hastened as much as possible to prevent changes in the sugar content. Should the filtration of the clarified solution be difficult and some time be consumed in obtaining a clear filtrate, it is better to throw away the solution and extract the sample again, as the results are very apt

to be incorrect. The few results in the following table will show the possible errors in such determinations:

RESULTS SHOWING ERRORS INTRODUCED BY SLOW FILTRATION.

Serial No.	Material.	Quick filtration.		Slow filtration and less speed.	
		Reduc-	Total	Reduc-	Total
		ing sugars.	sugars.	ing sugars.	sugars.
		Per cent.	Per cent.	Per cent.	Per cent.
7959	Wheat.....	0.18	1.73	0.32	2.05
	Mixed cattle feed.....	1.50	4.03	1.63	5.06
7894	Molasses feed.....	5.98	9.07	6.77	10.40

The more time consumed from the point of clarifying to that of determining the reducing sugar, the greater will be the error. Determinations were made on the fresh extract and on the extract that had stood over night after clarification.

A few of the results are given in the following table:

• DATA SHOWING EFFECT ON RESULTS OF STANDING OVER NIGHT.

Serial No.	Sample No.	Immediate determination.		Standing over night.	
		Reduc-	Total	Reduc-	Total
		ing sugars.	sugars.	ing sugars.	sugars.
		Per cent.	Per cent.	Per cent.	Per cent.
7856-B	1	0.23	1.86	1.66	3.83
7856-C	2	0.38	2.42	1.72	2.22
7856-A	3	0.42	3.30	2.41	3.73
7893	4 Corn meal.....	0.17	1.98	1.23	2.25
7894	5 Molasses feed....	5.98	9.05	10.21	11.50
8207	Alfalfa ¹	1.58	1.60	2.80	2.63
8209	Alfalfa and corn ¹ .	1.97	3.86	3.65	4.90

Standing over night in all cases greatly increased the reducing sugar content. In some instances this increase was over 500 per cent. The total sugars in all except one case (No. 7856-C) showed a marked increase, but the percentage increase is far below that of the reducing sugars. From the last two tables it is seen that allowing the solution to stand for any length of time after clarification increases the percentage of sugars present. This increase is due, no doubt, to enzymic action; the inhibiting agent having been neutralized, the enzymes again become active.

Time is an important factor in chemical analysis, as a chemist is often called away from his work and the solution in consequence stands for some time. It is well, therefore, to have a method that will allow of such delays without seriously affecting the results. When using the sodium carbonate digestion method such a lapse of time will certainly introduce an error, and it is readily seen that only the results which have been obtained by following very closely the procedure as outlined can be relied upon.

ALCOHOL DIGESTION METHOD.

The limitations of the sodium carbonate do not seem to apply in the case of the alcohol method. No substance need be added to the alcohol to destroy or inhibit the enzymes, as the alcohol itself and also the heat of extraction effects this. Hudson and Paine² have lately found that the enzyme invertase is de-

¹ U. S. Dept. Agr., Bureau of Chemistry, Bull. 107, (revised), 241.

¹ Lead acetate as a clarifier.

² U. S. Dept. Agr., Bureau of Chemistry, Circ. 58.

stroyed by 50 per cent. alcohol. After the enzymes are killed there is little chance of the extract changing on standing except through outside contamination. Church and Straughn¹ in their corn work have many times analyzed a portion of the fresh alcoholic extract and then shipped the remainder of their extract to be examined later. Results in all cases have been comparable, and the samples in some cases have been stored for from four to eight months before analysis. The alcohol method as given on page 487 indicates two or three points at which the work can be stopped and as much as a day or more elapse without fear of introducing any error. This is of great importance to the chemist who is called upon to make other determinations at the same time and who is liable to be called away from his work at any time. The natural acidity of the sample in this method does not play as important a part as in the other one. It is obvious, however, that if digestions of strongly acid substances are to be made the material should be neutralized. Again, if the alcohol used is strongly acid, it also should be neutralized.

DUPLICATING RESULTS.

Some methods will yield duplicate results when the determinations are carried on side by side that may not give concordant results when used at another time.

DUPLICATE ANALYSES MADE AT DIFFERENT TIMES BY THE SODIUM CARBONATE METHOD.

Serial No.	Number of analysis.	Reducing sugars. Per cent.	Total sugars. Per cent.
7856-A	First.....	0.24	3.28
	Second.....	0.23	3.07
	Third.....	0.51	2.91
7856-B	First.....	0.23	1.86
	Second.....	0.38	1.94
7900	First.....	3.41	32.36
	Second.....	3.52	31.74
7934	First.....	7.11	11.37
	Second.....	6.57	11.46
8049	First.....	1.88	34.36
	Second.....	2.16	35.79
8207	First.....	1.40	1.48
	Second.....	1.58	1.60

The results by the alcohol method show possibly a little better agreement, as given in the following table:

DUPLICATE ANALYSES MADE AT DIFFERENT TIMES BY THE ALCOHOL METHOD.

Serial No.	Number of analysis.	Reducing sugars. Per cent.	Total sugars. Per cent.
7856-A	First.....	0.00	2.99
	Second.....	0.00	2.93
	Third.....	0.00	3.00
7900	First.....	2.54	28.82
	Second.....	2.81	28.97
7934	First.....	5.72	10.12
	Second.....	5.82	10.47
8049	First.....	1.81	33.65
	Second.....	1.73	33.32
7959	First.....	1.46	3.91
	Second.....	1.57	3.99
	Third.....	1.55	4.15

¹ Bull. 127.

on the same sample. This is often noted when uncontrollable conditions which affect the results are present, or when the details of the manipulation are not accurately described in the method. When an extraction is to be made and the extract analyzed, questions of temperature and length of time of extraction are important. The latter point is generally taken into account by chemists, but temperature is not always considered unless special note is made of it. Directions to conduct extractions at room temperature are rather vague, for this temperature during the summer varies from that during the winter; and, again, some chemists prefer to work at a much lower temperature during the winter than others, and this plays an important part in the process. However, in the sodium carbonate method, the time, two and one-half hours, with occasional shaking, has been found long enough to remove the sugars under nearly all temperature conditions.

When using the greatest of care with the sodium carbonate method the results of determinations made at different times on the same sample seem to show a fair degree of agreement, as shown by the foregoing results.

TERMS USED IN STATING RESULTS.

As bearing on the general subject of sugar determinations, a word should be said regarding the methods of stating sugar results on such products as cattle feeds and grains. Some chemists calculate the reducing sugars to dextrose and some to invert sugar, while others state the reducing power in terms of metallic copper reduced by a given weight of the material under examination. The expression of the results in terms of sugars is more definite than in terms of copper reduction, which gives no clear idea of the amount present. Indeed, it is doubtful whether the reducing action noted is due to one particular sugar; it may be due to a mixture of several sugars or to invert sugar which is a mixture of equal parts of dextrose and levulose. In only a very few cases have the sugars been separated and identified. Therefore, for general work it seems that sugars before inversion should be reported as "reducing sugars calculated as dextrose" or "reducing sugars calculated as invert sugar," depending on which calculation was made. And for sugars after inversion the same phraseology should be used, namely, "total sugars calculated as dextrose" or "total sugars calculated as invert sugar." The increase in reducing sugars after inversion may not be caused entirely by the inversion of sucrose, but may be due to other compounds or sugars being split up into reducing sugars by the acid. It is well known that the ordinary inversion methods will hydrolyze other sugars, for instance, raffinose, and may hydrolyze such compounds as inulin or some of the glucosids and pentosans, forming reducing sugars. Under such circumstances it is certainly wrong to calculate the increase in reducing sugars as sucrose without a more definite knowledge of these sugars, although a part of this increase may be due to sucrose.

In order to eliminate a number of these compounds and restrict the increase to one or two sugars, the in-

vertase inversion method proposed by Hudson¹ should be used conjointly with the acid inversion. Under such circumstances, should the quantity of total sugars agree by both methods, one may safely say, with our present knowledge, that the increase in reducing sugars is due to sucrose, raffinose, or both. As the latter sugar is present in notable quantities in cottonseed-meal, and may be in other materials, it is not altogether safe to calculate this increase as sucrose with the idea that only sucrose is present. By the invertase method many other substances are eliminated. It seems better, therefore, to use the expressions (1) "reducing sugars calculated as dextrose," or "reducing sugars calculated as invert sugar;" (2) "total sugars by acid hydrolysis (or by invertase) calculated as dextrose," or "total sugars by acid hydrolysis (or by invertase) calculated as invert sugar," and (3) "increase in reducing sugars by acid hydrolysis (or by invertase) calculated as sucrose."

SUMMARY.

A method of preparing an extract for sugar determinations in grains, cattle foods, and vegetable material in general is given on page 487, depending on boiling the product with 50 per cent. alcohol. A comparison of the results obtained by this method using various classes of materials is given with that of a method depending on the extraction of the sugars with water at room temperature to which a percentage of sodium carbonate is added to inhibit enzymic action. A study of the limitations of the two methods is made, in which it is shown that the alcohol method will give satisfactory and comparable results on material, whether it is analyzed immediately or after standing for some time, while to obtain true and concordant results with the sodium carbonate method the most careful attention must be given to certain details of manipulation. In the sodium carbonate method, after neutralizing the sodium carbonate by clarifying with alum or lead, the work must be carried on with dispatch: (1) the enzymes again become active; (2) the acidity of the sample must be determined and the quantity of sodium carbonate thereby regulated, or the accuracy of the results will probably be affected; (3) normal lead acetate should be used instead of alum for clarification under most circumstances, otherwise an error is introduced. Taking these points into consideration, it is the opinion of the authors that the alcohol method is to be preferred in general work, but when a long, comparable series of results is to be obtained on samples of the same kind of material the sodium carbonate method might be used advantageously, provided it is run with dispatch and the greatest care is exercised in its operation; and, most important of all, the results obtained by its use should compare with those obtained by alcohol digestion. Some materials, however, can not be analyzed by the sodium carbonate method because clear filtrations are not obtainable even with lead clarification.

¹ U. S. Dept. Agr., Bureau of Chemistry, *Circ.* 50; *THIS JOURNAL*, 2, 43-5 (1910).

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THE DETECTION OF SALICYLIC ACID.

By H. C. SHERMAN AND A. GROSS.

Received May 8, 1911.

For the detection of salicylic acid, especially when present in small amounts, it is customary in many laboratories to rely upon the violet reaction with ferric chloride, almost to the exclusion of other tests. The popularity of the ferric chloride test is readily explained by its simplicity and delicacy. Using fresh one per cent. ferric chloride as reagent the test is delicate in our hands to a dilution of about 1 : 400,000 when applied to 10 cc. of solution, about 1 : 750,000 to 1 : 1,000,000 if 25 cc. of solution be tested. The violet color obtained with such small amounts of salicylic acid must be observed quickly as it fades rapidly, passing through a rose-red color. A faint rose color may also be obtained on addition of ferric chloride to solutions containing salicylic acid in amounts too small to show violet reaction.

Unfortunately, however, the formation of a violet color with ferric chloride is a reaction by no means confined to salicylic acid. Mulliken's tables¹ include many colorless compounds which give more or less distinctly violet reactions with ferric chloride and some of these also resemble salicylic acid in solubilities. That this may lead to error in the testing of foods for salicylic acid has been pointed out by several writers.²

Among the tests for salicylic acid, other than the ferric chloride reaction, are the formation of the methyl ester or the nitro-compound, the reactions with bromine water and with Millon's reagent, and the Jorissen test.

The adoption by Mulliken of the methyl-ester and nitration tests for the identification of salicylic acid is sufficient evidence of their value for cases in which enough salicylic acid is involved to make them available; but these tests and also the test with bromine water seem not to be sufficiently delicate for the detection of very small amounts.

In tests with Millon's reagent it was found that heating for some time increases considerably the delicacy of the test. When two drops of Millon's reagent were added to the solution to be tested, shaken in a test-tube, and immersed in a boiling-water bath with a blank test for comparison there was developed in the course of 45 minutes' heating a delicate reddish or pink color even in the presence of only minute amounts of salicylic acid. With practice and with blank tests for comparison no difficulty was found in detecting the presence of 1 part salicylic acid in 2,000,000 of water when 20 cc. were tested; when only 10 cc. were tested, the pinkish tint was barely perceptible at this dilution. Longer heating and variations in the amount of reagent added were tried without appreciably altering the result. The limit of delicacy

¹ "The Identification of Pure Organic Compounds."

² Brand, *Ztschr. f. d. ges. Brauw.*, 15, 303; *Ber.*, 27, 806; Erich, *Der Bierbrauer*, 24, 465; Munsche, *Woch. f. Brauerei*, 10, 739; Abraham, *Journ. de Pharmacie de Liège*, 5, 173; Backe, *Annales des Falsifications*, Nov., 1909; Sherman, *THIS JOURNAL*, 2, 24; Backe, *Compt. rend.*, 150, 540; 151, 78.

of the test with Millon's reagent as here used seems, therefore, to be reached by heating in boiling water for 45 minutes and to lie at a dilution of about 1 : 2,000,000.

The Millon reaction also has the advantage over the ferric chloride test that the color produced even with very small amounts of salicylic acid shows no evidence of fading on standing over night; but on account of the large number of substances which respond to the Millon reagent¹ it seems unlikely that this reaction will prove as useful as that of Jorissen.

The Jorissen reaction² has been used by a number of European investigators³ for the identification of small amounts of salicylic acid and was found useful by one of us⁴ as a means of distinguishing between salicylic acid and maltol or isomaltol when present in small quantity in foods.

In further experiments with this reaction we have found that by diminishing the amount of copper used and increasing the time of heating, the test can be made much more delicate than appeared in our earlier work in which the test was used in its original form, and considerably more delicate than the ferric chloride reaction. The longer heating is necessary to fully develop the characteristic color, at least when only very small amounts of salicylic acid are present, and the reduction in the amount of copper diminishes the slight green color due to the reagent which otherwise may interfere with the more delicate tests.

The test as now used for very small amounts of salicylic acid is as follows: Bring the solution to be tested into a test tube, add 4-5 drops of 10 per cent. sodium or potassium nitrite, 4-5 drops of 50 per cent. acetic acid, and 1 drop of one per cent. copper sulphate. Shake after addition of each reagent and finally place in a boiling-water bath in such position that the test liquid is completely immersed in the boiling water and allow to stand for 45 minutes, then remove, allow to cool and examine against a white background, viewing the tube both vertically and horizontally and comparing with a blank test in which the same amounts of reagents have been added to pure water.

In this way, the presence of as little as 0.005 to 0.01 milligram of salicylic acid in pure water solution can be detected. Faint but perceptible reactions were obtained with 5 to 8 cc. of a solution of 1 : 1,000,000 and with 18 to 25 cc. of solutions of 1 : 3,000,000 to 1 : 3,500,000.

No advantage has been found in a brine-bath over a water-bath, in longer heating than 45 minutes, nor in varying the amounts of nitrite and acetic acid used. When larger amounts of salicylic acid are present a drop of stronger copper sulphate solution may be used,

up to a ten per cent. solution as originally recommended. Except with very small amounts of salicylic acid the red color of the Jorissen reaction develops quickly on heating and the long immersion in the water-bath then becomes unnecessary if only qualitative results are required.

A feature which will be of great importance in colorimetric estimations of small amounts of salicylic acid is that while the violet color of the ferric chloride test fades rapidly, the red color of the Jorissen test is quite stable. Even the faint colors obtained by long heating, where only very minute amounts of salicylic acid are involved, have shown no deterioration when allowed to stand over night.

It has also been found that the ferric chloride and Jorissen tests may be applied to the same solution of salicylic acid. After making the ferric chloride test the liquid may be diluted until the violet color disappears and then submitted to the Jorissen reaction, when, if salicylic acid is present, pink color will appear.

No extended study seems to have been made to determine what other substances will give red or pink reactions in the Jorissen test. Jorissen, in describing his reaction, stated that phenol behaves in the same way as salicylic acid but benzoic acid does not. Allen states that neither benzoic, cinnamic nor tartaric acid responds to the Jorissen test, which statement we have confirmed.

Special importance attaches to the behavior in the Jorissen test of those substances which give violet reaction with ferric chloride. Maltol and isomaltol have already been considered; a few others have been tested with the following results:

Phenol, in our hands, gives the same color as salicylic acid in both the Millon and the Jorissen tests, but the limits of delicacy are quite different. Phenol can be detected by the Millon reaction to about 1 : 2,000,000. In the Jorissen test, phenol 1 : 100,000 gives practically the same color as salicylic acid 1 : 1,000,000.

Saligenin gives, in the Jorissen reaction, a red color at 1 : 10,000; a yellowish tint at 1 : 100,000; no reaction at 1 : 1,000,000. The limit of delicacy for the ferric chloride reaction with saligenin lies between 1 : 10,000 and 1 : 20,000.

2-oxy-isophthalic acid gives the Jorissen reaction up to a dilution of 1 : 100,000 but is easily distinguished from salicylic acid in the color which it gives with ferric chloride.

Methyl-ethyl-aceto-acetate, which gives, with ferric chloride, a violet-red color in concentrated solutions, gives neither the Millon nor the Jorissen reaction when tested at a dilution of 1 : 1,000.

Orcin, arbutin, resorcin and phlorizin, which give blue, violet, or red-violet reactions with ferric chloride do not respond to the Jorissen test.

THE PRESERVATION OF EGGS.

By R. BERGER.

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While the preservation of eggs on a commercial scale by the cold storage system is universally adopted,

¹ Vaubel, *Ztschr. angew. Chem.*, **1900**, 1125; Nasse, *Pflüger's Archiv. f. d. ges. Physiol.*, **83**, 361 (1901); Mann, "Physiological Histology," pp. 321-23, and "Chemistry of the Proteids," p. 7.

² Jorissen, *Bulletins de l'Academie Royal des Sciences, des Lettres, et des Beaux-arts de Belgique*, 3rd series, **3**, 259.

³ da Silva, *Compt. rend.*, **131**, 423; Klett, *Pharm. Centr.*, **41**, 452; *Ztschr. Unters. Nahr. Genussm.*, **4**, 469; Portes and Desmoulières, *Annal. chim. anal.*, **6**, 401; *Ztschr. Unters. Nahr. Genussm.*, **5**, 468; Windisch, *Ibid.*, **8**, 447.

⁴ Sherman, *THIS JOURNAL*, **2**, 24.

this method, for obvious reasons, is not well adapted for the consumer or small producer. To meet the needs of the latter, many experiments have been made to discover a method by which the best results might be obtained, and as a result the conclusion has been reached that immersion of freshly laid eggs in silicate of soda solution is the most efficacious.¹

In recommending silicate of soda solution, the fact that brine, as well as solutions of other antiseptics are employed in preserving eggs for technical purposes, such as for tanneries, etc., has not been ignored. These latter solutions, however, do not keep the eggs palatable, as they penetrate and contaminate them. On the other hand, silicate of soda, because of its colloidal nature, does not penetrate the egg membrane, its characteristic action being to close the pores of the shell.

In order to substantiate this hypothesis, I have experimented with many different substances, colloids as well as crystalloids, and while I found that many colloids, such as starch, gelatine, tannic acid, gum arabic, albumen, silicic acid and norgine,² were not absorbed by the lime shell, other colloids, as well as some crystalloids, were thus absorbed, all of these absorbed substances having an alkaline reaction. Caustic soda solution, however, penetrates the eggs very readily, causing the albumen to coagulate in a very few days. Many eggs, when immersed in a 5 per cent. solution of caustic soda, cracked within the first 24 hours, owing to the rapidly increasing pressure, while the others, not thus affected, increased about 2.5 per cent. in weight within a week.

As the closing of the pores of the shell by the action of silicate of soda causes the eggs to crack, when exposed to heat, many tests have been made to ascertain the length of time in which this closing of the pores takes place, and it was found that a solution of 1 volume commercial silicate of soda, 40° Bé., and 15 or 20 volumes of water, will close the pores within three to seven days, lime water being fully as effective in this respect. Sodium aluminate and castile soap acted somewhat slower, a solution of 1 part of the former in 15 parts of water requiring from 2 to 3 weeks, and a 1 to 20 solution of the latter about a month. Other solutions which close the pores are those of bicarbonate, di-, and especially trisodium phosphate. A 3 per cent. solution of barium hydrate acted much slower than lime water, although the latter contains only about 0.14 per cent. hydrate of lime. The concentration is of great influence. For instance, if 1 volume of silicate of soda be diluted with 120 volumes of water, none of the eggs would crack within a period of fifteen days.

Various writers differ somewhat in their opinions as to the relative merits of different preservatives, and difference in the quality of silicate of soda has also been considered as the cause of some of the

variations in the results obtained. I have accordingly experimented with eggs in crystallized silicate of soda, or "alkasil," $\text{Na}_2\text{O} \cdot \text{SiO}_2 \cdot 9\text{H}_2\text{O}$,¹ and four grades of commercial silicate of soda (supplied by courtesy of The Grasselli Chemical Company), varying practically between the formulas $\text{Na}_2\text{O} \cdot 4\text{SiO}_2$ and $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$. I have furthermore added caustic soda, and also lime, to silicate of soda high in SiO_2 , in order to bring down the SiO_2 percentage, and no great difference was found in regard to the pore-sealing action of these different actions. However, the weights of the eggs increased in the crystallized silicate of soda, the increase ranging from 0.6 per cent. in one week to 2 per cent. in five weeks, and similar increase in weights of eggs results when the latter are immersed in commercial silicate of soda, in which the SiO_2 percentage has been decreased by the addition of caustic soda, or lime, to such an extent that only 3 molecules or less of SiO_2 are in combination with 2 molecules of Na_2O in the solution. Moreover, while the weights of a great number of eggs, preserved in silicate of soda, remained constant within very close limits, the increases in the weights of eggs preserved in lime water, and especially in silicate of soda with a low percentage of SiO_2 , varied considerably. Alkasil does not, of course, keep eggs palatable, but it is interesting to note that they can be preserved in a caustic soda solution, if sufficient silicate of soda be added to have at least 2SiO_2 for $1\text{Na}_2\text{O}$ in solution.

To form an opinion on the permeability of the shells of preserved eggs, I kept a number of the latter in the open air for several weeks, and found that they would still crack when boiled. After 6 months in the atmosphere, their average loss in weight was only 6 per cent. against nearly 20 per cent. on unpreserved eggs. (Vaselined eggs showed no loss.)

DIRECTIONS FOR PRESERVING EGGS IN SILICATE OF SODA.

1. Use clean receptacles of glass, earthenware, wood or of most any material, if same is paraffined inside, and can be sealed hermetically. I found $\frac{1}{2}$ gallon screw cap glass jars, which will hold 14 or 15 eggs, most satisfactory, and in every way advisable.

2. Common silicate of soda, a sirup thick liquid of 40° Bé. or over, gives good results. It should be kept well sealed by paraffined or vaselined paper, pasteboard or cork stopper, or other cover impermeable to air and moisture, to prevent it from gelatinizing. Glass stoppered bottles, however, should not be used, as a little silicate may find its way to the ground neck, and it will then be impossible to remove the stopper later on, as silicate of soda will cement the stopper to the neck of the bottle.

3. The water should be pure, boiled water being preferable.

4. One part of silicate of soda to be very thoroughly mixed with 10 to 15 parts, or 1 part powdered silicate dissolved in 30 parts water, this solution to be well cooled before immersing the eggs therein.

¹ U. S. Dept. Agric., *Farmers' Bulletins* Nos. 103, 128, 273 and 287. "Das Huehnerei als Nahrungsmittel und die Konservierung der Eier," by Strauch, Bremen, 1897; "Les divers procédés de conservation des Oeufs," by R. Nourissé (Paris), 1907.

² E. Schmidt, "Zur Kenntniss der Norgine," *Chem. Ztg.*, 1910, p. 1149-1150.

¹ F. J. G. Beltzer, *Rev. gén. chim.*, 18, Oct., 1909.

5. The eggs must be clean, with strong, sound shells. They should be put into the preserving fluid, if possible, the same day they are laid, especially in summer. Unfertilized eggs are not likely to spoil, even if they are not so fresh. However, it is one of the strongest points of this preserving method that fertilized eggs will keep perfectly well, if the above precautions are taken. (Incubation is said to start on fresh, fertile eggs, if they are kept for about 24 hours at a temperature of at least 80° F., but if the proper incubating temperature—about 102.5° F.—is not reached soon and maintained, the egg germs will die and cause the eggs to decay.)

6. As soon as the eggs are packed in the preserving liquid, the receptacle is to be carefully sealed with a paraffined or vaselined paper or pasteboard, or with a screw cap or other reliable and tight cover. This is necessary not only to prevent water from volatilizing, which would finally expose the upper eggs to the atmosphere, but also to prevent the carbonic acid of the air from decomposing the silicate.

7. The eggs packed in the well sealed jars should be stored in a cool place, especially at first, that is, before the egg germs have lost their vitality. However, the temperature must not drop below the freezing point.

THE EFFECT OF THE ENVIRONMENT OF CARBONATED BEVERAGES ON BACTERIA.¹

By C. C. YOUNG AND N. P. SHERWOOD.

Received April 4, 1911.

There is a tradition among bottlers of carbonated soft drinks, founded as far as can be learned on very little experimental data, that the conditions under which "soft" drinks are prepared are toxic to all bacteria.²

The basis of this idea appears to be statements in the literature which state that carbon dioxide under pressure markedly reduces the number of bacteria in water and that *B. typhosus* and *B. coli* show a reduction of 90 per cent. in 24 hours when exposed to carbon dioxide under pressure. However, the experiments that were available were not carried out under bottlers' conditions. The conception held by the majority of manufacturers is that so long as the water is clear and sufficiently soft to carbonate well, no thought need be given to its sanitary quality, as the carbon dioxide under pressure will kill any living organism.

It was the object of this investigation to find whether or not any pathogenic organism could withstand the unfavorable environment of the bottled carbonated beverages a sufficient length of time to reach the consumer.

Investigations of trade conditions showed that, with the possible exception of ginger ale, most of the "pops" put on the market are consumed within ten days from the time of bottling. In fact during the summer months many instances were found where the goods

¹ Paper read before the Kansas City Section, Amer. Chem. Soc., March 25, 1911.

² Sulz, "A Treatise on Beverages," p. 67; Karl F. Kellerman, *Plant Bulletin*, 100, Part 8, page 7; "Sterilization of Water by Citric Acid," *Scientific American*, 98, 201, March 21, 1908.

go directly from under the bottling machine to the consumer.

The following experiments were carried out under trade conditions, with the one exception, however, that all conditions were intensified.

Pop bottles of 240 cc. capacity and ability to withstand 20 pounds' pressure were used. All bottles except the ones to be inoculated with *B. typhosus* were washed in the usual manner; the latter were washed, boiled for 30 minutes and cooled. Several sets of bottles giving different conditions of environment were inoculated. Three sets, of eight bottles each, were inoculated from 48-hour broth cultures of *B. typhosus*, *B. coli communis* and *B. prodigiosus*, respectively, each bottle receiving 1 cc. of its respective culture. Syrup known as bottlers' lemon had been previously added. Four bottles from each of the three sets were then filled, in the usual manner, with carbonated water at 18 pounds' pressure, at 10° C., and capped. The remaining four bottles in each of the three sets were filled, in the usual manner, with uncarbonated water and capped.

In the fourth and fifth sets no organism was used for inoculation, syrup was added to one but not to the other, and both were filled with carbonated water and capped. A sample of the water used in bottling was also taken. Samples from each set were plated out in the University laboratories 4, 28, 80 and 244 hours after the filling of the bottles. All bottles were kept at room temperature to correspond with normal conditions in trade. In plating, plain agar was used for *B. prodigiosus*, both plain and litmus-lactose agar for *B. coli*, and litmus-lactose agar for *B. typhosus*. Litmus-lactose agar was used to aid in identification of the last-named organisms. Plates of *B. prodigiosus* were incubated at room temperatures and those *B. coli* and *B. typhosus* at 37½° C. *B. prodigiosus* was identified by its characteristic red pigment. Presumptive and confirmatory tests were used for *B. coli*. Agglutination in the hanging drop and the Widal reaction were used in identifying *B. typhosus*. The mean results obtained are tabulated below:

TABLE I.
CARBONATED WATER USED

Duration of exposure before examination.	With syrup.				Without syrup. Not inoculated.
	<i>B. typhosus</i> , No. per cc.	<i>B. coli</i> , No. per cc.	<i>B. prodigiosus</i> , No. per cc.	Not inoculated, No. per cc.	
0 hours	200,000	950,000	850,000	300	20
4 hours	25,000	250,000	800,000
28 hours	9,000	20,000	250,000
80 hours	1,200	1,300	150,000
244 hours	110	900	5,000	150	0

TABLE II.
UNCARBONATED WATER USED

Duration of exposure before examination.	With syrup.			Without syrup. Not inoculated.
	<i>B. typhosus</i> , No. per cc.	<i>B. coli</i> , No. per cc.	<i>B. prodigiosus</i> , No. per cc.	
0 hours	200,000	950,000	850,000	20
4 hours	200,000	950,000	850,000	...
28 hours	50,000	(**)	(**)	...
80 hours	6,000	100,000	(**)	...
244 hours	900	40,000	110,000	200

(**) Slipped.

From the above tables we may note the following facts and conclusions:

1. That the number of organisms outside of those introduced was extremely small.

2. That there was a decided reduction in number of the organisms introduced, owing to standing 244 hours uncarbonated.

3. That there was a very marked reduction in numbers of all three organisms introduced, and especially of *B. typhosus*, owing to conditions existing in the carbonated bottles.

4. That there was not a complete killing out of the organisms introduced, during the entire experiment.

5. That *B. prodigiosus* and *B. coli* seemed to be somewhat more hardy than *B. typhosus*.

Undoubtedly¹ the longevity of *B. typhosus* depends in a great measure upon the virulence of the organism, and as the results above show that some of the organism will live longer than the beverage is normally on the market, the manufacturer should not depend upon the percentage of reduction caused by the carbon dioxide and other substances used.

From the observation that the most hardy individuals can resist these adverse conditions for a considerable length of time, the logical conclusion is that no water should be used in the manufacture of a carbonated drink, that is, in the least suspicious, and if a doubtful water is the only source of supply, this should be subjected to treatment by some method of sterilization with subsequent filtration through a trustworthy and efficient filter.

KANSAS UNIVERSITY WATER LABORATORIES.

THE COMPOSITION OF THE APPLE AS AFFECTED BY IRRIGATION.

By C. E. BRADLEY.

Received April 1, 1911.

Coöperating with the horticultural department of this Station in connection with their irrigation inves-

year, a summary of which is herewith given. The samples were selected from the Station experimental plats in the Willamette and Rogue river valleys and were taken at the proper stage for picking. Analyses were made as soon as possible after picking, usually within two or three days.

In preparing samples, the apples were peeled and cored and then run through a small meat grinder and the ground product placed in sealed jars. Samples for analyses were weighed out soon after grinding before juice and pulp separated.

Moisture was determined in a vacuum oven at 75-80° C. and 20-25 inches vacuum.

For sugars, 2½ times the normal weight of pulp was placed in a 250 cc. graduated flask, 10 cc. lead sub. acetate added, made up to 200 cc. with water, and the flask shaken for several hours in a shaking machine. This shaking was found necessary to completely remove the sugars from the pulp. The flask was then made to mark. Reducing sugars were determined in this solution by Allihn's method after removing lead with Na₂CO₃ and Na₂SO₄. Cane sugar was determined by the method of Clerget, the inversion being carried out in the cold according to official methods. For acid, 5-10 grams of pulp were weighed into a 200 cc. beaker, 100 cc. water added and the whole boiled for a few minutes, then titrated with N/10 NaOH, using phenolphthalein as indicator.

In the table of averages Nos. 1, 2, 4 and 5 represent results of checks made on the same orchard so that all conditions except moisture supply are uniform. It will be noted that the irrigated samples are somewhat higher in moisture and consequently lower in solids than samples from the dry checks. Also that the irrigated apples contain higher percentages of sugar based on dry material. Apples from irrigated plats were in general larger than those from the unirrigated. Individual apples from a given plat showed very little variation among themselves and results from single

AVERAGE COMPOSITION OF IRRIGATED AND UNIRRIGATED APPLES.

		Irrigated.											Acid as malic. Per cent
		Original.					Dry Material.						
No.	Description.	Solids. Per cent.	Red sugar. Per cent.	Cane sugar. Per cent.	Total sugar. Per cent.	Ash. Per cent.	Acid as malic. Per cent.	Solids. Per cent.	Red sugar. Per cent.	Cane sugar. Per cent.	Total sugar. Per cent.	Ash. Per cent.	
1	Newtowns.....	16.17	7.21	4.64	11.85	0.27	0.62	100.00	44.58	28.69	73.27	1.66	3.83
	Medford.....												
2	Spitzenburgs...	17.60	8.41	5.77	14.18	0.29	0.51	100.00	47.77	32.77	80.54	1.64	2.90
	Medford.....												
3	Newtowns.....	15.23	7.29	4.62	11.91	0.22	0.80	100.00	47.86	30.33	78.19	1.44	5.25
	Medford.....												
Non-irrigated.													
4	Newtowns.....	18.98	7.38	4.73	12.11	0.32	0.96	100.00	38.87	24.91	63.78	1.68	5.06
	Medford.....												
5	Spitzenburgs...	18.81	4.59	0.28	100.00	24.40	1.48	...
	Medford.....												
6	Newtowns.....	15.67	6.27	4.23	10.50	0.25	0.70	100.00	40.00	26.99	66.99	1.59	4.46
	Corvallis.....												
7	Spitzenburgs...	16.92	6.37	5.84	12.21	0.25	0.75	100.00	37.64	34.51	72.15	1.47	4.43
	Corvallis.....												

tigations a large number of analyses of apples have been carried out in this laboratory during the past

apples agreed well with those obtained from composite samples.

¹ Expert Testimony, Chicago Drainage Canal Case. *Water Supply Paper No. 194*; Whipple, *Engineering Record*, 1904, p. 746; Houston, *Fourth Report Royal Commission*, 3, 20-58 (1904).

The protein content of the peelings tested averaged 0.70 per cent. while that of the edible portion was

0.20 per cent. Only traces of starch were present in the samples tested.

Credit is due Mr. L. A. Bundy and Mr. B. Pilkington for the analytical work involved in these investigations.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPT. AGRICULTURE, BY PERMISSION OF THE SECRETARY.]

THE EFFECT OF LOW TEMPERATURES ON GROUND CHICKEN MEAT.¹

By H. W. HOUGHTON, PH.D.

Received April 26, 1911.

INTRODUCTION.

While low temperature, as a means of preserving food, was familiar to the early settlers in this country, and was extensively practiced by them, it is only within comparatively modern times that the possibilities of this addition to the conveniences of modern civilization have been fully developed.

The earliest and most primitive form of cold storage was that of mother earth herself. Ice, as a means of preservation, was unknown in Colonial days, and the early pioneer sought to preserve his food by placing it in a cave. Where natural facilities were lacking, artificial caves or cellars were resorted to.

It was not until the latter part of the eighteenth century that the more progressive husbandmen resorted to ice, cut from neighboring streams and ponds, as a means of refrigeration, and so slowly did the new method find favor that it was not until 1805 that the first large house was built for the storage of natural ice. From this time, however, the trade grew by leaps and bounds, reaching its largest proportion in the period between 1860-1870.

To-day the demand for ice has become so great that the natural product is not sufficient, and the yield of the lakes and streams is supplemented with ice frozen by mechanical means.

As ice became more commonly used, careful study was given to the best means of utilizing it. The earliest method, and that still used in shipping poultry, fish, and oysters, was to bring the ice in direct contact with the article to be preserved. A more modern device is that of a chilled chamber whereby the food is kept cold without touching the ice.

But while the methods of cold storage above outlined were adequate to meet the needs of individual families or small communities, they were not sufficient to supply the ever-growing demand for food preservation. To meet this demand mechanical refrigeration has been introduced. The use of ice on a large scale has been abandoned, and in its place the large storage rooms are cooled by the frozen surfaces of pipes containing brine or ammonia. These rooms are utilized for the storage of animal and plant products at various temperatures ranging from below 0° to 40° F. This modern method has been found greatly superior to the old system in that the tem-

perature can be controlled more readily and held at any desired point, while at the same time a drier atmosphere is produced.

The growing needs of our civilization, and the ever-increasing localization of the food-producing area has made refrigeration on a large scale a vitally important factor in the life of the people. The distances between the large manufacturing cities in the East and the centers of food production in the central and western parts of the country make the proper preservation of foodstuffs a matter of extreme importance to the nation.

In supplying this preservation the refrigeration plants and cars have proved of great benefit. The advantages obtainable, however, are frequently abused. The consumer is placed at the mercy of the merchant, for the latter many times purchases a large supply of perishable food at a low price and places it in cold storage until higher prices can be obtained. This is practiced particularly in the case of game, which is held in cold storage from one Christmas to the next in order that the merchant may derive a larger profit. Then if there occurs a rise of temperature, necessitating a rapid sale of foodstuffs, the merchant, rather than sacrifice his profit, again places his stock in cold storage, to be sold when an opportune time arrives, and this process may be repeated for years. Not only game, but likewise all other varieties of human food, derived from the animal kingdom, are similarly held for sufficient storage periods to allow the merchants to demand fancy prices for articles which were purchased by them when the market was oversupplied. Then again, the increase of the sale of ice cream is so great on holidays that a large quantity is reserved in cold storage from one to five weeks in advance to meet the enormous demand for the one day.

It is only natural, therefore, that with the growth of its benefits and abuses, careful studies have been made and accurate data have been compiled as to the effect of refrigeration on several of the most important articles of consumption.

The purpose of the present investigation is to study the chemical changes occurring in ground chicken meat when placed in cold storage at from -6° to +6° F., with and without the presence of carbon dioxide. The experiments covered a period of five months, samples being analyzed monthly throughout the time. The investigation includes the separation and detection of the common enzymes. No effort, however, has been made in these experiments to determine the effect of such refrigeration on the activity of these enzymes.

HISTORICAL.

In 1872 M. Tellier,² reported that meat stored at from -2° to +3° C. retained its fresh qualities.

In 1874 Bouley² experimented with Tellier's process of refrigeration and concluded that meat stored for two months at from -2° to +3° C. developed a peculiar fatty odor that affected the flavor; that desiccation and oxidation occurred in the exposed portion of the fat and meat frozen for several months;

¹ A thesis submitted to the George Washington University for the degree of Doctor of Philosophy.

that there was produced a protein compound that did not exist in the muscular tissue during life; lastly, that while a small part of the albuminoids disappeared, there were formed leucomaines, lactic acid, and a trace of alcohol. Pogziale, and a little later, in 1889, a commission appointed by the French Minister of War confirmed Bouley's conclusions.

In 1892, Grassman³ observed no harmful change or any loss in nutritious food value in pork and beef due to storage at temperature of -2° to -4° C.

In 1897, Gautier⁴ reported from his investigation of mutton and beef, stored for from five to six months at below zero, a slight loss of moisture, accompanied by an increase of digestible albuminoid materials. An increase of peptone in the frozen meats indicated the presence of a trypsin-like ferment.

In 1900, Glage⁵ stated that the maturation of meat preserved in chilled rooms was due to the existence of certain bacteria in the rooms. He arrived at the conclusion that in many cases the flora of the meat was similar to that of milk and cheese and that these bacteria play a part in the maturation of meat.

In 1901, C. Mai⁶ claimed that by proper chilling treatment putrefactive changes could be prevented, but that the action of ferments or enzymes still continued to some extent and either directly or indirectly caused the changes which take place in the so-called ripening of meats.

In 1903, Müller⁷ reported that if the temperature of the cold storage room is 2° or 3° C. the maturation of meat due to ferments went on, but putrefaction was prevented. The reaction of the living muscle was neutral, but it became acid when the myosine coagulated and the hardening of the muscle appeared. Accompanying the disappearance of the muscular striations, there was produced an abundant formation of granulations.

König⁸ made a summary of analyses of chicken meat by Stützer, Moleschott, König, Kranch, Allen-

dorff, Atwater, and Wood. As mean percentage values for the flesh of chickens, König gives the following:

Water.....	72.22
Protein.....	21.33
Fat (by difference).....	4.55
Nitrogen-free extract.....	0.75
Ash.....	1.15

In 1906, Grindley⁹ reported that the general appearance of undrawn refrigerated poultry was similar to that of fresh fowl, except in one respect, namely, a characteristic flavor that was not due to putrefaction but perhaps, as Müller states, to the ripening of the meat.

At the same time Bird¹⁰ made a practical test with drawn and undrawn turkeys. He hung the fowls, during the month of February, in the open air and found that at the end of the first week the undrawn turkey was perfectly sound while the drawn one showed distinct signs of decay.

In 1908, Higley¹¹ reported that the edible portions of healthy poultry, either fresh or cold-stored at 5° C., contained no harmful bacteria, toxins, or ptomaines.

During the same year H. W. Wiley¹² and his co-workers made an extensive investigation of the effect of cold storage on eggs, quail, and chickens. In these experiments the chemical, microscopic, bacteriological, histological, and organoleptic examinations of eggs, quail, and chickens, stored six months or more, gave results which differed entirely from those obtained by the examination of the fresh materials. With the exception of the chemical analysis the results indicate very clearly that the changes in eggs, quail, and chickens are recognizable after about six months in storage. The chemical analyses are given in the following tables.

At the same time that Dr. Wiley and his associates made their preliminary report, Richardson¹³ read a paper on "The Criteria of the Deterioration of Flesh

PERCENTAGE COMPOSITION OF FRESH CHICKEN MUSCLE.

Number.	Sample.	Kind of meat.	Water.	Fat.	Ash	Protein (N \times 6.25).	Kreatin (N \times 3.11).	Total solids.	Sum of constituents determined.
66	Plymouth Rock broiler.....	{ Light	75.50	0.49	1.17	23.46	1.10	24.50	97.92
		{ Dark	71.75	2.40	1.21	21.40	0.827	28.25	101.33
67	Plymouth Rock young roaster or broiler....	{ Light	75.73	0.17	1.33	21.84	1.01	24.27	100.08
		{ Dark	75.86	1.38	1.49	21.07	0.64	24.14	100.44
73	Plymouth Rock roaster.....	{ Light	73.30	0.51	1.24	22.52	0.920	24.70	100.92
		{ Dark	74.48	2.88	1.18	20.69	0.743	25.52	99.97
78	Rhode Island Red roaster.....	{ Light	73.56	0.98	1.26	23.50	1.01	26.44	100.31
		{ Dark	73.02	2.99	1.35	23.13	0.64	26.99	101.13
86	Rhode Island Red large roaster.....	{ Light	75.01	0.53	1.21	21.95	1.02	24.99	99.13
		{ Dark	75.94	2.15	1.13	19.77	0.796	24.06	99.78

PERCENTAGE COMPOSITION OF COLD STORAGE CHICKEN MUSCLE.

Number.	Time of storage. Months.	Kind of meat.	Water.	Fat.	Ash	Protein. (N \times 6.25).	Kreatin. (N \times 3.11).	Total solids.	Sum of constituents determined.
84.....	14	{ Light	73.67	0.27	1.10	23.01	1.16	26.33	99.21
		{ Dark	72.16	1.93	1.27	23.16	0.852	27.85	99.37
85.....		{ Light	72.22	0.27	1.14	24.36	1.10	27.78	99.16
		{ Dark	70.09	2.85	1.25	24.55	0.877	29.91	99.61
69a.....	24	{ Light	74.43	0.40	0.95	23.00	0.836	25.57	99.61
		{ Dark	73.11	2.04	1.07	22.78	0.761	26.89	99.76
79.....		{ Light	72.60	0.83	1.06	25.10	0.569	27.40	100.15
		{ Dark	69.52	2.93	1.21	25.50	0.715	30.48	99.87
82.....	48	{ Light	71.42	0.48	1.39	24.78	0.945	28.58	99.01
		{ Dark	67.10	3.80	1.35	26.28	0.914	32.90	99.44
83.....		{ Light	65.87	0.19	1.48	26.91	1.41	34.13	95.86
		{ Dark	65.48	3.10	1.59	27.00	0.801	34.52	97.97

Food" in which the author laid special emphasis upon the value of the determination of ammoniacal nitrogen.

Toward the close of the year 1908, Richardson and Scherubel¹⁴ made a chemical investigation of fresh and frozen beef. The chemical analyses indicated no marked difference between the percentage of nitrogenous compounds in the cold water extract of fresh beef and of beef frozen 554 days.

A subsequent paper by the same authors¹⁵ considered the cold storage of beef at temperatures above freezing point. In this article it is shown that in the case of beef kept at from 2° to 4° C. the analysis of the cold water extract showed a gradual increase of total solids, total nitrogen, albumose, meat base nitrogen, ammonia, and acidity in direct proportion to the increasing age and decomposition.

In 1909, Emmett and Grindley¹⁶ investigated the effect of cold storage on beef and poultry stored 22 and 43 days. They concluded that the slight changes that occurred did not alter the nutritive value of the meat. Pennington¹⁷ included in her report on "Studies of Poultry from the Farm to the Consumer" a review of the scientific work done in the United States on this subject, a statement of the industrial application of refrigeration to the handling of dressed poultry and eggs, based on a careful study of existing conditions, and a very suggestive section on the application of the scientific data so far obtained to industrial uses.

The knowledge of chicken fat is at present rather unsatisfactory. In 1897 Amthor and Zink¹⁷ reported the following tables as the results of their observations on both fat and the free fatty acids:

Chicken fat, specific gravity.....	0.9241
Melting point.....	33.40° C.
Solidifying point.....	21.27° C.
Iodin number.....	66.7
Saponification number.....	193.5
Reichert number.....	1.0
Acetyl number.....	45.2
Acidity (fresh).....	1.2
Free fatty acids, specific gravity at 15° C.....	0.9283
Melting point.....	30.40° C.
Solidifying point.....	32.34° C.
Iodin number.....	64.6
Saponification number.....	200.8

In 1903, Zaitscheck¹⁸ analyzed the fat of two chickens, one of which had been fed on corn and the other on corn and milk. His results are as follows:

ANALYSIS OF FAT FROM CORN-FED AND MILK AND CORN-FED CHICKENS.

Determinations.	No. 1.	No. 2.
	Corn-fed.	Corn- and milk-fed.
Specific gravity at 30° C.....	0.9129	0.9153
Melting point.....	36.0° C.	38.5° C.
Solidifying point.....	17.4° C.	22.0° C.
Melting point, free fatty acids.....	37.0° C.	39.5° C.
Solidifying points of free fatty acids.....	34.5° C.	35.5° C.
Refraction at 40° C.....		
Saponification number.....	214.0	216.8
Non-volatile fatty acids.....	95.3	94.8
Iodin number of fat.....	70.6	57.6
Iodin number of fatty acids.....	54.4	45.4
Volatile fatty acids.....	0.88	0.88
Free fatty acid calculated as oleic.....	0.40	0.49

PLAN OF EXPERIMENT.

Thirty-six carefully selected and milk-fed Plymouth

Rock chickens were purchased from a reputable dealer who killed, picked and packed them with ice in my presence. After allowing the chickens to remain in contact with the ice six hours, the light and dark meat were separated from the skin, loose adipose tissue and bones, ground, and mixed by hand for fifteen minutes in order to obtain a uniform sample. The final mixture of each variety of chicken meat was divided into enough portions of 300 grams each to supply samples for the monthly investigations. Analyses of each variety were made immediately, while the remaining portions were placed in cold storage at a temperature varying from -6° to +6° F.

The analytical methods used in this investigation were selected after careful consideration of the literature. In each determination two or three results were obtained, the average figure being recorded. By the exercise of the utmost care and by close attention to the manipulation of the methods and the use of the very best obtainable apparatus, results have been secured from which conclusions can be drawn as to the chemical changes taking place in ground chicken meat at low temperatures.

In the following tables a distinction is made between chicken fat and chicken meat fat. The chicken fat was prepared by pressing the adipose tissue of the viscera. The chicken meat fat was prepared by extracting the dried meat with anhydrous ether. After completely removing the ether at the lowest possible temperature, the residue was used for analysis. The following analytical methods were used:

PREPARATION OF SAMPLE FOR CHEMICAL EXAMINATION.

Separate the sample as completely as possible from the bones and loose adipose tissue and pass it rapidly and repeatedly through a sausage mill until a thorough mixture and complete maceration are obtained. The sample must be kept on ice to prevent decomposition, and all of the determinations should be begun as soon as possible after the sample is prepared.

The determination of moisture, ether extract, total nitrogen, total sulphur and phosphorus were made according to the methods given in *Bulletin 107*, Revised Bureau of Chemistry, U. S. Department of Agriculture.

DETERMINATION OF FREE AMMONIA.

Place 5 to 10 grams of the chicken meat in a distillation flask with 500 cc. of water and 10 grams of light calcined magnesium oxide. Then connect the flask with a condenser and distil three successive 150 cc. of the liquid into tenth-normal hydrochloric acid. Titrate the residual acid with twentieth-normal sodium hydroxide. Calculate free ammonia from the result of the total distillation.

ANALYSIS OF THE COLD WATER EXTRACT.

PREPARATION OF EXTRACT.

Weigh duplicates of 20 grams of the chicken meat into 600 cc. Erlenmeyer flasks and add about 100 cc. of water containing chloroform. Shake the mass for two hours, after which filter it into a 500-cc. volumetric flask through cheese-cloth and wring it out by hand. After rinsing the hand with water, tie the meat loosely

in the cheese-cloth and repeatedly wash with 50 cc. portions until the amount of the water-soluble solution is 2000 cc. Filter the solution and preserve it with chloroform, being careful always to use the same variety of filter paper. If not, the analysis will vary to such an extent that any comparison will not be correct. The first 500 cc. of extract contains 91 per cent. of the total water-soluble nitrogen and practically the entire amount of coagulable nitrogen.

ACIDITY.

Measure 100-cc. portions of the cold water extract into beakers and titrate against tenth-normal caustic soda, using phenolphthalein. Express the acidity as lactic acid.

TOTAL NITROGEN.¹⁹

Measure out duplicate samples of 100 cc. and determine the nitrogen by the modified Gunning method.

COAGULABLE NITROGEN.

Measure out duplicate samples of 100 cc. of the cold water extract into beakers, place on the steam bath, and evaporate to 25-cc. volumes. (As no change in the acidity of chicken meat occurred while in cold storage, the solutions were not made neutral.) Filter the coagulable nitrogen, wash it thoroughly, and determine the nitrogen in the residue on the filter paper by the modified Gunning method.

AMINO ACIDS.

Make up filtrates from the determinations of coagulable nitrogen to the same volumes and cool to 12° C. Add 50 cc. of a 24 per cent. tannic acid solution and 6 grams of salt. Keep these solutions at 12° C. for twelve hours with frequent shaking. Filter, allowing filter to drain thoroughly, and determine nitrogen in the filtrates by the modified Gunning method. Correction is made for the previously determined free ammoniacal nitrogen and the nitrogen contained in the amount of tannin salt solution used.

PROTEOSES AND PEPTONE.

Deduct from the total water-soluble nitrogen the sum of the coagulable nitrogen, amino acid, and free ammonia of the cold water extract.

FREE AMMONIA IN COLD WATER EXTRACT.²⁰

Measure 500 cc. of water-soluble solutions into a

1000-cc. round distilling flask, add 10 grams of magnesium oxid, and distil ammonia into 5 cc. of tenth-normal hydrochloric acid, and filtrate the residual acid with twentieth-normal sodium hydroxide.

WATER-SOLUBLE SOLIDS AND ASH.

Evaporate 100 cc. of cold water extract in platinum dishes to dryness at the temperature of boiling water, place in a water oven, dry to constant weight, and weigh. Char and extract with water, filter, and ignite filter and residue to white ash. Add filtered portion, evaporate to dryness, and ignite at a low temperature. The difference between the total water-soluble solids and the water-soluble ash will give the water-soluble organic matter.

VOLATILE SULPHUR COMPOUNDS²¹ (SULPHUR DIOXIDE, HYDROGEN SULPHIDE, HYDROSULPHIDE, THIO ESTERS.)

Weigh 25 grams of the meat into a beaker. After thoroughly mixing, place the contents of the beaker in a 1000-cc. round-bottom distilling flask, to which are added 500 cc. of water and 1 cc. of sirupy phosphoric acid. Connect the flask with a condenser which is so arranged as to collect the distillate in standardized alkali. After distilling over 300 cc. in a current of CO₂ (to prevent oxidation of the sulphur compound during distillation) determine the unneutralized standardized alkali. After adding bromine, evaporate the distillate to dryness and burn to a white ash. Dissolve residue in water, make slightly acid with hydrochloric acid and filter. After washing the filter paper thoroughly, determine the sulphates present as barium sulphate.

ANALYSIS OF FAT.

The determination of specific gravity, refractive index, iodine number, saponification number, soluble acids, Hehner number and free fatty acids are made according to methods in *Bulletin 107*, Revised, Bureau of Chemistry, U. S. Dept. of Agriculture.

PREPARATION OF FATTY ACIDS FROM FAT.²²

Saponify a quantity of fat by boiling 50 grams with 40 cc. of caustic potash solution (specific gravity 1.4), and 40 cc. of alcohol in a porcelain dish on a water bath with constant stirring until the soap be-

ANALYSES OF CHICKEN MEAT DURING A STORAGE PERIOD OF FIVE MONTHS.

LIGHT CHICKEN MEAT.

(All figures on basis of original meat.)

Length of storage. Days.	Moisture. Per cent.	Ash. Per cent.	Ether extract. Per cent.	Free ammoniacal nitrogen.		Total solids. Per cent.	Ash. Per cent.	Organic extractives. Per cent. (by difference).	Total nitrogen. Per cent.	Cold water extracts.				
				Per cent.	Per cent.					Coagulable nitrogen. Per cent.	Proteoses and peptone. Per cent.	Amino acid. Per cent.	Ammoniacal nitrogen. Per cent.	Acidity as lactic acid. Per cent.
0	69.33	1.18	6.71	3.74	0.021	4.79	1.17	3.62	0.858	0.305	0.144	0.387	0.022	1.08
30	68.92	1.15	6.97	3.73	0.035	3.98	1.06	2.92	0.585	0.014	0.060	0.483	0.028	0.99
61	68.35	1.18	7.07	3.64	0.032	5.25	1.19	4.06	0.714	0.075	0.089	0.522	0.028	0.99
90	68.86	1.12	6.92	3.82	0.038	6.05	1.08	4.97	1.008	0.144	0.308	0.514	0.042	1.08
118	68.64	1.15	6.85	3.68	0.029	5.50	1.15	4.35	0.994	0.178	0.258	0.527	0.031	1.17
150	68.77	1.13	6.80	3.73	0.039	5.92	1.09	4.83	1.001	0.266	0.159	0.541	0.035	1.08

DARK CHICKEN MEAT.

0	71.76	1.14	5.74	3.43	0.019	4.89	1.18	3.71	0.641	0.252	0.167	0.203	0.019	0.72
30	71.39	1.07	6.22	3.37	0.032	3.36	1.00	2.36	0.417	0.007	0.070	0.323	0.017	0.54
61	71.16	1.11	6.30	3.44	0.021	3.93	1.08	2.85	0.490	0.051	0.089	0.329	0.021	0.63
90	70.85	1.18	6.14	3.47	0.027	4.08	1.01	3.07	0.602	0.170	0.019	0.389	0.024	0.81
118	70.62	1.18	6.26	3.48	0.024	4.26	1.18	3.08	0.637	0.187	0.036	0.375	0.019	0.72
150	70.68	1.16	6.17	3.24	0.026	4.50	1.08	3.42	0.588	0.217	0.052	0.298	0.021	0.63

TABLE I (Continued)
Calculated to moisture- and ash-free basis
Cold water extracts

Length of storage, Days	Total nitrogen, Per cent	Ammoniacal nitrogen, Per cent	Total solids, Per cent	Organic extractives, Per cent	Total nitrogen, Per cent	Organic extractives, Per cent	Proteins and peptides, Per cent	Amino acids, Per cent	Ammoniacal nitrogen, Per cent	Acidity as lactic acid, Per cent
0	18.42	0.092	21.05	15.89	3.75	1.54	0.602	1.79	0.096	4.74
30	18.28	0.102	18.71	11.07	1.86	0.063	0.265	1.30	0.122	4.33
61	18.55	0.137	20.43	17.55	3.58	0.120	0.368	2.23	0.120	4.25
90	18.54	0.164	26.19	19.80	4.56	0.625	1.53	1.20	0.162	4.84
118	18.78	0.118	18.54	18.80	4.25	0.761	1.10	1.20	0.133	4.88
150	18.90	0.187	15.41	20.73	4.29	1.14	0.662	1.31	0.150	4.30

DARK CHICKEN MEAT										
Length of storage, Days	Total nitrogen, Per cent	Ammoniacal nitrogen, Per cent	Total solids, Per cent	Organic extractives, Per cent	Total nitrogen, Per cent	Organic extractives, Per cent	Proteins and peptides, Per cent	Amino acids, Per cent	Ammoniacal nitrogen, Per cent	Acidity as lactic acid, Per cent
0	18.08	0.089	22.80	17.37	3.00	1.18	0.767	0.440	0.089	3.17
30	18.81	0.150	15.77	11.43	1.96	0.063	0.329	1.52	0.090	1.48
61	18.05	0.098	18.54	15.50	2.29	0.168	0.415	1.54	0.098	2.94
90	18.89	0.114	18.89	16.00	2.78	0.778	0.587	1.75	0.138	3.71
118	18.85	0.104	18.42	14.04	2.90	0.832	0.255	1.71	0.088	3.19
150	18.78	0.118	20.40	15.85	2.67	0.487	0.200	1.80	0.095	2.80

comes pasty. Dissolve the soap in 100 cc. of water, and boil the solution to evaporate the alcohol; this can be effected readily by replacing the water as it boils away. Next decompose the soap by means of dilute sulphuric acid. When by continued boiling the fatty acids have been obtained as a clear oily layer, free from solid particles, floating on the aqueous liquid, draw off the latter by means of a siphon and wash the fatty acids several times with hot distilled water until all the mineral acids have been removed. Since the fatty acids of lower molecular weight dissolve in hot water, and may redden litmus paper, methyl orange should be used to test for the complete removal of the mineral acid. Then place the dish containing the fatty acids on the water bath and

warm it until they are completely liquefied. The water and impurities will settle out and the warm acids may then be poured through a dry plained filter fitted in a hot water funnel. The fatty acids will thus be obtained sufficiently dry for examination. If they solidify at the ordinary temperature, it is advisable to allow the fatty layer to solidify, then to perforate the cake by means of a glass rod, pour off the acid liquid, and wash with hot water as before.

REFRACTIVE INDEX AND IODIN ABSORPTION NUMBER OF CHICKEN MEAT FAT

Length of storage, Days	Refractive index at 40° C	Iodin absorption number
LIGHT		
0	1.4550	39.92
30	1.4555	40.70
61	1.4560	44.58
90	1.4550	47.14
118	1.4515	52.23
150	1.4505	52.50
DARK		
0	1.4580	40.74
30	1.4670	41.15
61	1.4685	42.11
90	1.4645	50.00
118	1.4635	55.80
150	1.4630	53.00

ANALYSIS OF CHICKEN FAT

Determinations	Fresh	Exposed two weeks at room temperature	50 days storage
Specific gravity at 100° C	0.9002	0.8971	0.9013
Iodin number	58.77	58.48	58.80
Saponification number	195.50	196.75	195.47
Soluble acids as butyric acid	0.38	1.67	0.40
Holmer number	88.82	90.20	87.00
Free fatty acids as oleic	0.247	1.47	0.268
Free fatty acids			
Specific gravity at 100° C	0.8659	0.8715	0.8670
Iodin number	58.74	58.80	57.02
Saponification number	216.52	214.25

DISCUSSION.

The samples of chicken meat when taken from the freezer presented a slightly dried appearance on the exposed surfaces but the moisture content of these samples as compared with that of the original meat is not perceptibly changed. The same is true of the ash, ether extract, acidity, and total nitrogen. However, this lack of variation does not apply to every result found, especially in the cases of the nitrogenous bodies of the cold water extract, for in meat, when it

PER CENT OF SULPHUR AS SO₂ IN CHICKEN MEAT

(Calculated to moisture-free basis)

LIGHT CHICKEN MEAT			
Length of storage, Days	Total sulphur, Per cent	Soluble sulphur, Per cent	Volatile sulphur, Per cent
0	1.87	0.489	0.000
30	1.87	0.488	0.009
61	1.40	0.348	0.028
90	2.67	0.546	0.022
118	2.00	0.604	0.009
150	1.82	0.576	0.022

DARK CHICKEN MEAT			
Days	Per cent	Per cent	Per cent
0	3.65	0.200	0.000
30	3.30	0.379	0.000
61	3.50	0.937	0.045
90	3.50	1.060	0.044
118	3.47	1.090	0.030
150	3.45	1.020	0.034

PER CENT OF PHOSPHORUS AS P₂O₅ IN CHICKEN MEAT

(Calculated to moisture-free basis)

LIGHT CHICKEN MEAT		
Length of storage, Days	Total phosphorus, Per cent	Soluble phosphorus, Per cent
0	1.96	0.24
30	1.98	0.24
61	1.80	0.40
90	1.87	1.57
118	1.88	1.50
150	1.84	1.54

DARK CHICKEN MEAT		
Days	Per cent	Per cent
0	2.23	0.92
30	2.17	1.12
61	2.08	1.46
90	1.90	1.44
118	1.97	0.40
150	2.00	1.48

undergoes ordinary deterioration from enzymic and bacterial processes, there is a conversion of insoluble proteins into soluble forms and of coagulable forms into non-coagulable by the continued hydrolytic splitting of large molecules into smaller ones with the final production of amino acids, acid amides, lower fatty acids and ammonia. As a natural assumption from these alterations in the composition of the meat at low temperatures, the organic extractives of the meat would increase and thereby cause a slight increase of water-soluble nitrogen. In order, however, to understand more clearly the exact changes that occur, the individual determinations must be discussed.

The total solids of the cold water extracts of both light and dark chicken meat decreased remarkably the first thirty days though this change was more noticeable in the dark meat. This decrease seems to be caused by the initial effect of the cold temperature on the original coagulable nitrogen which showed a greater decrease than any of the nitrogenous constituents determined. Mr. Müller⁷ states that cold temperature coagulated the myosine and increased the acidity of meat. This seems evident from the marked decrease of the total solids in the cold water extracts of the four samples of chicken meat of the same origin. The gradual increase of total nitrogen after thirty days, in both varieties of chicken meat, is probably caused by the action of bacteria and enzymes upon the meat, forming substances which are soluble in water. These deteriorating agencies appear to be more active in the light chicken meat than in the dark, or else the light meat is less resistant to the action than the dark meat, for in the former the total solids of the cold water extract reached a higher per cent. after 91 days in cold storage than those of the cold water extract of the original chicken meat, while in the latter case the total solids of the cold water extract increased gradually for 150 days, when it is slightly lower than that of the cold water extract of the original meat.

At the beginning of the experiments the organic extractives²³ of both the light and the dark chicken meat are the same, after which the results are parallel to the total solids of the cold water extracts. As this result was obtained by subtracting the water-soluble ash, which was practically constant throughout, from the total solids, there is no need of its discussion.

The total sulphur, soluble sulphur, and total phosphorus were constant. But this constancy does not hold true of the water-soluble phosphorus and volatile sulphur. There was a gradual increase of water-soluble phosphorus in both varieties of chicken meat during the first 90 days of cold storage, after which it remained practically constant. This increase, more noticeable in the dark chicken meat, can be traced back to the action of bacteria and enzymes on the phosphorus-containing, organic compounds of the chicken meat. There is a similar increase in connection with the cold storage of eggs, in which Cook²⁴ found an increase of inorganic phosphorus with a corresponding decrease of organic phosphorus. The

volatile sulphur increased slightly with the length of time in cold storage; these changes can be considered as a significant indication that both varieties of chicken meat had deteriorated.

The increase of free ammonia in the light chicken meat signifies that that variety of meat deteriorated to a greater extent than the dark chicken meat, in which the free ammonia is practically constant. This increase of free ammonia in storage chickens has been obtained by Pennington and Greenlee²⁵ in their application of Folin's method and by Weber and Houghton²⁶ in their investigations of the incipient deterioration occurring in chickens stored six months. Like the organic extractives, the total nitrogen of the cold water extract of both varieties of chicken meat decreased during the first thirty days, followed by a gradual increase. The increase of the total nitrogen in the cold water extract of the light chicken meat is so rapid that after ninety days in cold storage a higher per cent. is observed than on the original sample. This increase of water-soluble nitrogen seems to be characteristic of light meat. It has been shown that the total nitrogen of the cold water extract of quail²⁷ preserved in cold storage increased with the time of storage, while in the water-soluble nitrogen of the meat of the entire chicken, in which the dark meat predominates, a slight decrease was indicated. As the majority of the meat of quail is light, the increase of water-soluble nitrogen in the light chicken meat here studied is confirmed. Chittenden and Cummins²⁸ observed that the light chicken meat was more digestible than the dark. Although there was a gradual increase of the total nitrogen in the cold water extract of the dark chicken meat after the first thirty days, nevertheless after 150 days the total water-soluble nitrogen was slightly less than that of the original sample. Richardson²⁴ has found that the total nitrogen in the cold water extract of beef, which is dark meat, does not change after the meat has been in cold storage 554 days.

The coagulable nitrogen runs directly parallel with the organic extractives, total solids, and nitrogen of the cold water extracts. The decrease of coagulable nitrogen of each variety of chicken meat, which occurred during the first thirty days, verifies further the fact that myosine is coagulated by the cold temperature. The gradual increase of coagulable nitrogen in both light and dark chicken meat after the first thirty days is probably caused by the action of bacteria and enzymes on the protein material of the chicken while in cold storage, forming new nitrogenous bodies which are coagulable.

The increase of proteoses and peptone in the light chicken meat is the result of the deterioration which this variety of meat has undergone, as has already been discussed. With the dark chicken meat there was a slight decrease of proteoses and peptones. The increase of amino acids in both varieties of chicken meat can be traced to the maturation of the meat. The free ammonia of the cold water extract is practically identical with the free ammonia of the meat itself.

The analyses of the chicken fat indicate no change during thirty days in storage.

The iodine number of the chicken meat fat increases regularly for both varieties of meat.

CARBON DIOXIDE AS A PRESERVATIVE OF ANIMAL FOOD.

So slight is the literature on this valuable factor in the solution of the proper preservation of perishable food, that the discussion can hardly be considered as being in more than a tentative stage. Prof. Gamgee,²⁸ the originator of the means of preserving perishable food, found that meat, contained in vessels in which the entire amount of air had been displaced by carbon dioxide, was preserved for given periods. The exact preserving efficiency of carbon dioxide was not investigated until recently. Frankel,³¹ Altana²⁹ and Bruschettini³⁰ experimented on the effect of carbon dioxide on organisms, drawing the conclusions that the action of strict anaerobic and of

certain mixed aerobic bacteria was prevented and that of other forms was retarded by this gas.

In this investigation the chicken meat was placed in an air-tight desiccator having an inlet and outlet tube through which the carbon dioxide could be permitted to flow into the desiccators in such a manner as to displace the entire quantity of contained air and not injure the cell body of the meat. The carbon dioxide was allowed to flow slowly into the desiccator for fifteen minutes. In order to thoroughly investigate this mode of preserving meat in direct comparison with the present study of the effect of cold storage on chicken meat, portions of the same light and dark chicken meat used in the experimental work just described were placed in five desiccators filled with carbon dioxide, thereby affording samples for complete monthly analyses. These desiccators were placed in a chill room (0° C.) after the first month, as the temperature of the refrigerator (12°–13° C.) was not constant. Using the methods previously stated, the following results were obtained:

ANALYSES OF CHICKEN MEAT COLD-STORED, USING CARBON DIOXIDE.

LIGHT CHICKEN MEAT.

(All figures on basis of original meat.)

Cold water extracts.															
Length of storage.	Moisture.	Ash.	Ether	Total	Free	Total		Organic	Total	Coagulable	Pro-		Amino	Ammo-	Acidity
Days.	Per cent.	Per cent.	Per cent.	nitro- gen. Per cent.	ammoniacal nitrogen. Per cent.	solids. Per cent.	Ash. Per cent.	extract- tives. Per cent.	nitrogen. Per cent.	nitro- gen. Per cent.	teose. and peptones. Per cent.		acids. Per cent.	niacal nitrogen. Per cent.	as lactic acid. Per cent.
0	69.33	1.18	6.71	3.74	0.021	4.79	1.17	3.62	0.858	0.305	0.144	0.387	0.022	1.08	
30 ¹	68.72	1.11	6.48	5.68	0.042	4.38	1.13	3.25	0.758	0.023	0.170	0.530	0.035	1.35	
61	68.45	1.12	6.25	3.74	0.049	5.08	1.11	3.97	0.885	0.046	0.202	0.595	0.042	1.26	
90	68.40	1.16	6.55	3.80	0.044	6.05	1.16	4.89	0.924	0.156	0.131	0.595	0.042	1.39	
118	68.69	1.11	6.73	3.76	0.036	5.80	1.08	4.72	0.980	0.252	0.161	0.530	0.037	1.26	
150	67.32	1.13	6.65	3.72	0.052	5.92	1.09	4.83	1.008	0.243	0.128	0.602	0.035	1.26	

DARK CHICKEN MEAT.

0	71.76	1.14	5.74	3.43	0.019	4.89	1.18	3.71	0.641	0.252	0.167	0.203	0.019	0.72
30 ¹	71.61	1.11	5.68	3.39	0.030	3.76	1.18	2.58	0.553	0.014	0.105	0.406	0.028	0.67
61	71.56	1.16	5.70	3.33	0.032	3.88	1.09	2.79	0.630	0.091	0.115	0.403	0.021	0.72
90	70.88	1.19	5.99	3.54	0.034	4.25	1.08	3.17	0.633	0.163	0.115	0.327	0.028	0.85
118	71.22	1.16	5.97	3.51	0.031	4.26	1.12	3.14	0.613	0.191	0.030	0.363	0.029	0.81
150	71.51	1.15	5.76	3.47	0.033	4.37	1.10	3.27	0.630	0.207	0.057	0.338	0.028	0.72

NITROGENOUS CONSTITUENTS OF CHICKEN MEAT COLD-STORED, USING CARBON DIOXIDE.

LIGHT CHICKEN MEAT.

(Calculated to moisture, ash, and fat-free basis.)

Length of average. Days.	Cold water extracts.				Total nitrogen. Per cent.	Coagulable nitrogen. Per cent.	Proteoses and peptone. Per cent.	Amino acids. Per cent.	Ammoniacal nitrogen. Per cent.	Acidity as lactic acid. Per cent.
	Total nitrogen. Per cent.	Ammoniacal nitrogen. Per cent.	Total solids. Per cent.	Organic extractives. Per cent.						
0	16.42	0.092	21.03	15.89	3.77	1.34	0.632	1.70	0.096	4.74
30 ¹	15.58	0.177	18.49	13.72	3.20	0.097	0.718	2.24	0.148	5.70
61	15.47	0.203	21.01	16.42	3.66	0.190	0.835	2.46	0.174	5.21
90	15.91	0.184	25.32	20.47	3.87	0.653	0.548	2.49	0.176	5.82
118	16.02	0.153	24.71	20.11	4.17	1.07	0.686	2.26	0.158	5.37
150	14.94	0.209	23.77	19.40	4.05	0.976	0.514	2.42	0.141	5.06

DARK CHICKEN MEAT.

0	16.06	0.089	22.89	17.37	3.00	1.18	0.782	0.950	0.089	3.37
30 ¹	15.70	0.139	17.41	11.95	2.56	0.065	0.486	1.88	0.130	3.10
61	15.43	0.148	17.98	12.93	2.92	0.422	0.533	1.87	0.097	3.34
90	16.13	0.155	19.37	14.45	2.88	0.743	0.523	1.49	0.128	3.87
118	16.21	0.143	19.68	14.50	2.83	0.882	0.139	1.68	0.134	3.74
150	16.08	0.153	20.25	15.15	2.92	0.959	0.264	1.57	0.130	3.33

¹ In refrigerator at 12° C.; remainder of experiment conducted in chill room at 0° C.

PER CENT. OF SULPHUR AS SO_4 IN CHICKEN MEAT COLD-STORED, USING CARBON DIOXIDE.
(Calculated to moisture-free basis.)
LIGHT CHICKEN MEAT.

Length of time stored. Days.	Total sulphur. Per cent.	Soluble sulphur. Per cent.	Volatile sulphur. Per cent.
0	2.67	0.489	...
30 ¹	2.49	0.416	0.013
61	2.54	0.444	0.038
90	2.34	0.570	0.031
118	...	0.639	0.025
150	2.45	0.520	0.027
DARK CHICKEN MEAT.			
0	3.65	1.20	...
30 ¹	...	1.16	0.017
61	3.34	1.02	0.028
90	3.37	1.10	0.044
118	3.61	1.09	0.031
150	3.59	1.08	0.031

PER CENT. OF PHOSPHORUS AS P_2O_5 IN CHICKEN MEAT COLD-STORED, USING CARBON DIOXIDE.
(Calculated to moisture-free basis.)
LIGHT CHICKEN MEAT

Length of storage. Days.	Total phosphorus. Per cent.	Soluble phosphorus. Per cent.
0	1.96	1.24
30 ¹	2.01	1.34
61	1.88	1.49
90	...	1.52
118	1.89	1.47
150	1.90	1.47
DARK CHICKEN MEAT.		
0	2.23	0.92
30 ¹	2.22	1.23
61	2.14	1.48
90	2.06	1.48
118	2.19	1.39
150	2.21	1.47

REFRACTIVE INDEX AND IODIN ABSORPTION NUMBER OF CHICKEN MEAT FAT COLD-STORED, USING CARBON DIOXIDE.

Length ² of storage. Days.	Refractive index at 40° C. LIGHT.	Iodin absorption number.
..	1.4660	39.92
30 ¹	1.4645	49.08
61	1.4660	45.78
90	1.4615	47.38
118	1.4610	47.92
150	1.4610	48.05
DARK.		
0	1.4680	40.74
30 ¹	1.4680	53.33
61	1.5685	52.00
90	1.4650	53.79
118	1.4630	53.03
150	1.4635	53.50

DISCUSSION.

The results of the experiments with carbon dioxide are so nearly identical with those obtained on the effect of low temperatures on chicken meat that it will be needless to enter into a discussion of them. There are, however, a few figures that verify the usefulness of carbon dioxide as a preservative of perishable foods.

The retarded increase of total water-soluble nitrogen of the cold water extract, accompanied by a rapid increase of proteoses, peptone and amino acids, is important in illustrating the inhibitory action of carbon dioxide upon bacteria.

If it is true that carbon dioxide has a retarding effect on the bacterial action in chicken meat, the

¹ In refrigerator at 12° C.; remainder of experiment conducted in chill room at 0° C.

changes that have occurred must be due to enzymes. However, to assure success in this method of employing carbon dioxide as a preservative of meat in refrigeration, there are three factors necessary: air-tight containers, complete displacement of the air without injuring the cell body of the meat, and a constant temperature below 12° C.

IDENTIFICATION OF ENZYMES IN GROUND CHICKEN MEAT.

Owing to the influence of the enzymic activity in animal tissue subjected to cold storage, it will be of interest to cite the investigations that have been recently made to identify the various enzymes present in animal tissues. The investigators who have contributed to the literature on this subject are Battelli, Frederic and Stein,^{32,33} Lob³⁴ and Mulzer,³⁵ Ville and Moitessier,³⁶ Kastle and Loevenhart,³⁷ Loew,³⁸ Bach,³⁹ Euler,⁴⁰ Shaffer⁴¹, van Itallie,⁴² Lesser,⁴³ Jolbauer and Zeller,⁴⁴ Ostwald,⁴⁵ Lockemann, Thies and Wichern,⁴⁶ Battelli and Stern,⁴⁷ Roaf,⁴⁸ Heffler,⁴⁹ Wakeman,⁵⁰ McCallum and Hart,⁵¹ Abelous and Gerard,⁵² Oppenheimer,⁵⁴ and Ranson.⁵⁵

The enzymes that have been detected in animal tissue are oxydase, peroxydase, catalase, protase, invertase, hydrolytic, nitrate reducing, phytin splitting, and glycolytic enzymes.

Each time the ground chicken was analyzed in the experiments just cited, an extract for the detection of enzymes was prepared. It was necessary to composite these residues since the extracts each month from the amounts of chicken that could be spared were insufficient to allow the tests to be made, in separating and detecting the enzymes the following methods were used:

PREPARATION OF EXTRACT FOR DETECTION OF ENZYMES.

The extract was prepared by extracting some of the finely ground meat several times with water saturated with chloroform. This extract was filtered and sufficient alcohol added to the filtrate to make a 60 per cent. solution. The liquid was shaken for half an hour and set aside for twenty-four hours, at which time an abundant flocculent precipitate had collected in the precipitating jar. The clear liquid was then siphoned off, the residue dissolved in water, and a solution of sodium phosphate and calcium chloride added until a heavy precipitate of calcium phosphate formed. This was allowed to settle, chloroform being added to prevent bacterial action. The clear liquid was again drawn off and the residue shaken up with water and filtered; this filtrate was dialyzed for twenty-four hours in running water; sufficient alcohol was then added to make an 80 per cent. solution and the mixture shaken violently for half an hour. The precipitate was allowed to settle for twelve hours and then filtered off, the precipitate being washed with 95 per cent. alcohol and dried. The powder thus obtained was of a light-brown color, soluble in water. The water solution of this powder was tested for enzymes as follows:

Oxydase.—To 5 cc. of a 5 per cent. solution of gum guaiacum in alcohol was added, drop by drop, the

solution to be tested, a boiled portion of the solution to be tested for enzymes being used as a check. No blue color was given by either the heated or unheated showing the absence of oxydase.

Peroxydase.—To 5 cc. of a gum guaiacum solution a few drops of hydrogen peroxide were added and then, drop by drop, the solution to be tested. Both kinds of meat gave a deep blue color, indicating the presence of peroxydase, while some of the boiled solution, when added to guaiacum extract, gave a brownish color, showing that peroxydase had been destroyed by boiling.

Protase.—A 10 per cent. solution of gelatin was prepared, thymol being added to prevent the interference of bacteria, and the solution was rendered slightly opaque by the addition of calcium carbonate. This was distributed in sterile tubes, approximately 5 cc. in each tube, and cooled rapidly to prevent the calcium carbonate from settling. Five cc. of 0.5 per cent. meat enzyme solution, containing a few drops of toluol, were added to gelatin tubes and these tubes set aside at room temperature for 24 hours. The gelatin was acted upon to some extent. In the check, which contained some of the boiled enzyme solution, the amount of gelatin remained constant.

Upon acidifying a portion of the enzyme solution, so that it contain 0.20 per cent. of HCl, and by making another portion alkaline with sodium carbonate and then testing the action of these solutions on gelatin tubes, the alkaline solution becomes more active. These results indicate an enzyme similar to trypsin.

Invertase.—Ten cc. of 10 per cent. cane sugar solution were added to 5 cc. of 0.5 per cent. enzyme solution, some toluol added, and the solution examined with a polariscope, then set aside at 38.5° C. for 12 hours and again tested with the polariscope, which showed the presence of invertase.

Lipase.—To 10 cc. of ethyl butyrate solution were added 5 cc. of meat enzyme solution containing some toluol; this mixture was set aside at 38.5° C. for 12 hours and the acidity determined, using phenolphthalein as indicator. The acidity was not increased.

Diastase.—Five cc. of a 0.5 per cent. of meat enzyme solution were added to a 1 per cent. starch solution, toluol added, and the mixture set aside in an incubator at 38.5° C. for 24 hours. The solution was then tested for reducing sugars by heating with Fehling's solution. There was no reduction in either case.

Catalase.—To 40 cc. of a solution of meat enzyme, containing 5 grams of enzyme powder to 100 cc. of water, 5 cc. of hydrogen peroxide solution were added and the amount of oxygen given off was measured. In thirty minutes a measurable amount of oxygen was given off. The check, which was a boiled solution of the enzyme, gave no oxygen when treated with hydrogen peroxide. This indicates that the enzyme solution has the properties of catalase.

Nitrate-reducing Enzyme.⁵⁰—One-tenth of a gram of the enzyme powder was mixed with 25 cc. of a 1 per cent. potassium nitrate solution and set aside at

35° C. for two hours. Test clear solution with naphthalene hydrochloride solution and sulphonilic acid solution as given in Mason's "Water Analysis." A pink color indicated nitrites reduced by enzyme.

GENERAL CONCLUSIONS.

Chicken meat subjected to cold storage, even for a period of five months, showed certain physical and chemical changes which clearly demonstrated that it is not identical with fresh material.

The cold storage meat felt soft in marked contact to the firmness of the fresh chicken meat, and a slight characteristic odor was detected.

The chemical changes that apparently take place in the cold-stored meat by direct comparison with the original chicken meat are: (1) slight variations of moisture and ether extract; (2) a small increase of ammonia, especially in the case of the light chicken meat; (3) a decided increase of water-soluble nitrogen, total solids, and organic extractives in the light chicken meat, with a slight decrease of the same constituents in the dark meat; (4) a decrease of coagulable nitrogen in both varieties of chicken meat during the first thirty days, followed by a rise which did not reach that of the fresh sample; (5) an increase of amino acids in both kinds of chicken meat with an increase and decrease of the proteoses and peptones respectively in the light and dark chicken meat.

An increase of soluble phosphorus was indicated during the first 90 days of the storage period, which was more marked in the dark meat than in the light meat. In the cold-stored samples a little volatile sulphur was found, none being detected in the fresh meat. The analyses of chicken fat indicated a fairly constant composition, but in the chicken meat fat of the cold-stored chicken the iodine number increased regularly while the index of refraction decreased slightly.

The alteration particularly noticed in the light meat was inhibited to a certain extent by storing in an atmosphere of carbon dioxide, accompanied by an increased production of proteoses, peptones, and amino acids. The initial increased production of these nitrogen bodies is probably due to enzymic action during the first 30 days at 12° C.

The enzymes detected were peroxydase, catalase, protase similar to trypsin, invertase, and a nitrate-reducing enzyme.

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PLANTS AND MACHINERY.

AN ELECTRICALLY CONTROLLED CONSTANT TEMPERATURE WATER BATH FOR THE IMMERSION REFRACTOMETER.

By H. C. GORE.

The water bath of the immersion refractometer must be held within narrow limits at 17.5°C .—3 temperature usually below that of the room. It is therefore cooled by the addition of cold water. Admitting tap water or ice water at a constant rate is unsatisfactory, as constant adjustment is required by changes in room temperature. The device herein described, by which water is added to the bath automatically, has given satisfaction during a period of

many months. No claim to originality can be made, in view of the many devices of this kind which have been proposed.

The tap water runs through the sight tube A (Fig. 1) and is diverted to the bath when the rubber tube B is closed by the lever of the sounder C. In warm weather the water is cooled by passing it through the copper coil D, immersed in ice water in the vessel E. The refractometer bath F is provided with an overflow pipe, K, and is stirred by a current of air entering through a tube not shown; E and F are insulated by magnesia packing to prevent the condensation of moisture which occurs during warm humid weather.

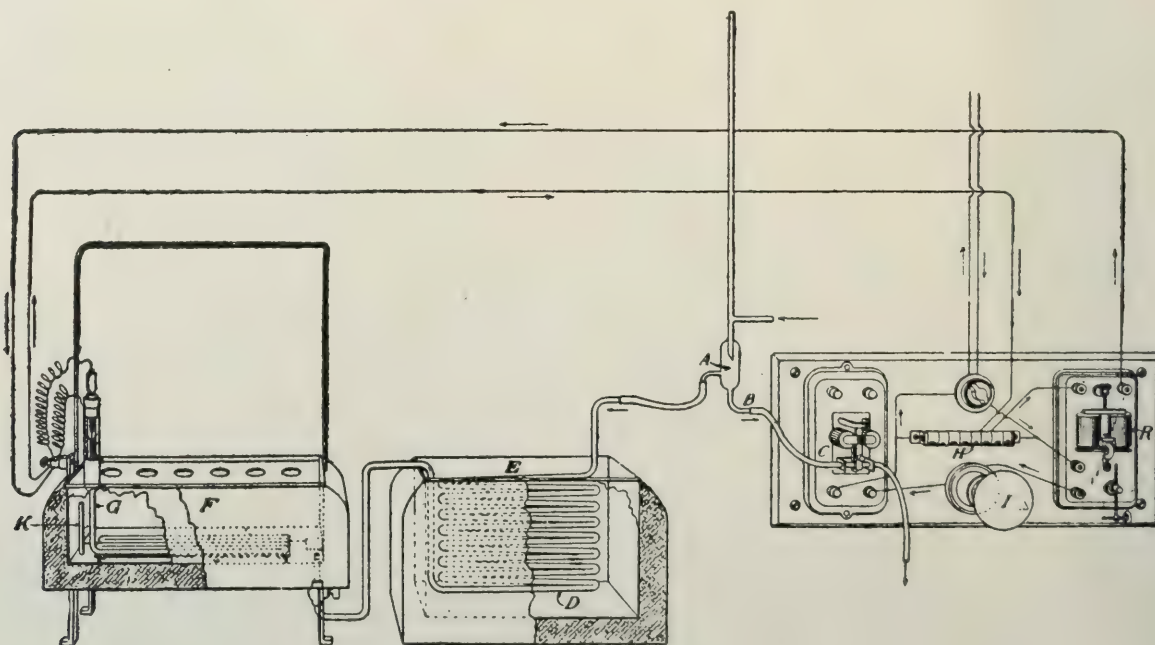


Fig. 1.

The thermostat G consists of a long glass tube bent into a flat rectangular coil and fastened to a perforated brass plate resting on short legs on the bottom of the bath. It is filled with mercury and closed at one end. To the open end is sealed a device shown in detail in Fig. 2. Electric connection is made with the mercury in the thermostat through the platinum wire A (Fig. 2) which passes through the glass wall near the double seal. The low tension current which is made and broken in the thermostat at B which operates the relay R (Fig. 1) is taken as a shunt from the 110-volt direct-lighting current by connecting the low-tension across adjacent taps on the 1,000-ohm resistance coil H. There are seven such taps along the coil and the potential difference between two adjacent ones is about 14 volts when the coil is in the 110-volt circuit. The current which actuates the sounder is made and broken by the relay. It passes from the relay through the 32-candle power lamp I, then through the electromagnets of the sounder, and back to the line, using the 110-volt direct current. The sounder is of the usual form, rated at 5-ohms, and heats but very slightly when the current passes through continuously. Except for the simple device shown for supporting the rubber tube, no other change in the sounder is necessary except that, if desired, the edges of the lever may be beveled so that the rubber tube is closed more easily. Small condensers, not shown, situated in the bases of the sounder and relay are used in lessening sparking when the currents are opened and closed in the thermostat and the relay respectively.

If cooling water is added at a rate very slightly more rapid than is necessary, the temperature is controlled with great exactness. Under these conditions, however, not enough cool water would be supplied should the room temperature rise considerably. On the other hand, if cold water is added too rapidly the bath becomes much undercooled at each addition. It has been found well so to regulate the supply that water is added to the bath about half the time. The temperature is then controlled within 0.1°C ., irrespective of changes in room temperature.

AN APPARATUS FOR CONTINUOUS SAMPLING OF CONDENSER WATERS FROM EVAPORATORS.

By GEORGE P. MEADE.

Received May 16, 1911.

Mr. R. S. Norris, in his article on "The Determination of Sugar Lost by Entrainment from Evaporators" in *THIS JOURNAL*, October, 1910, gives the following method of sampling condenser waters. "Five liters of condenser water are collected, a liter at a time, at

intervals of half an hour, as it leaves the condenser and as near to it as possible."

This method of intermittent sampling is the one usually employed. It will give a fairly satisfactory sample where entrainment in multiple effects is being studied. However, in the case of vacuum pans, in which the quantity and the viscosity of the boiling material are constantly changing, such a sample may fail to be representative.

The writer has devised an apparatus by means of which a sample may be taken continuously throughout any convenient period. It has been used successfully for two years. The accompanying print shows the arrangement.

"A" is the leg pipe of the condenser of the evaporator. "B" is a quarter-inch pipe entering the leg pipe near the top. "C" is a second quarter-inch pipe entering at any convenient point below the lowest level at which the water column in the leg pipe will stand when the evaporator is in use. These quarter-inch pipes project into the leg pipe about two inches. This prevents rust and dirt from the sides of the condenser from washing into the sample. "D" and "E" are heavy glass carboys. They are connected as shown in the small drawing. All connections must be air-tight.

When the valves on "B" and "C" are opened the sampling apparatus becomes a part of the vacuum system. The condenser water is forced through "C" into the carboy "D" by the pressure of the column of water in the leg pipe above "C." By manipulating the valves the water may be made to flow into "D" in a full stream or drop by drop as desired. "E" serves as a trap to catch any water from the upper pipe when the vacuum is broken.

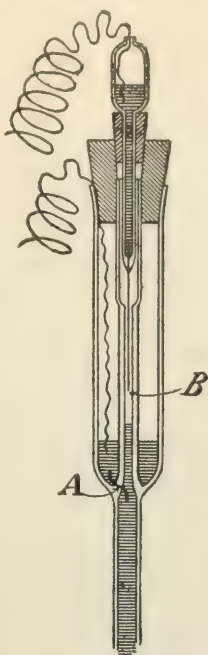
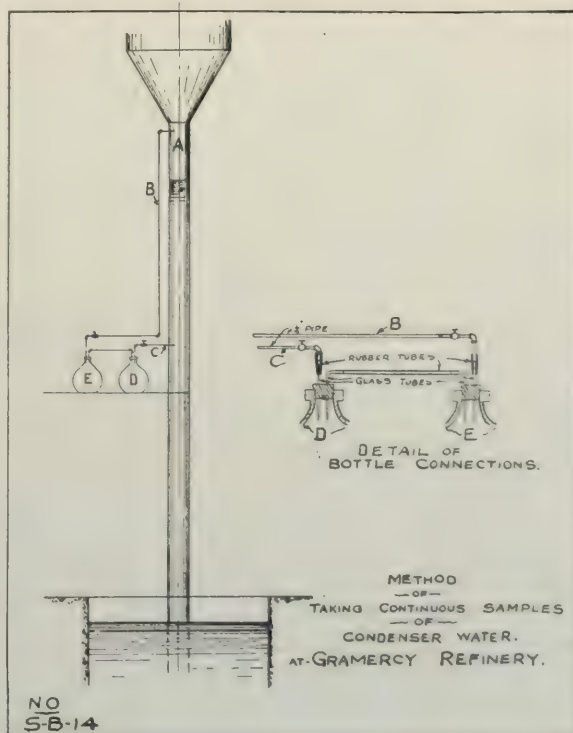


Fig. 2.



The sample will stop running when the vacuum is broken but it will start again when the vacuum is sufficient to lift the column of water in the leg pipe above the level of "C."

Preparatory to taking a sample the rubber connection between "C" and "D" should be broken and the end of "C" immersed in a little clean water. The valve is then opened. The water will be drawn through the pipe and will clear it of rust and dirty water.

The carboys used must be carefully selected. There is danger of a serious accident if they are not sufficiently heavy to withstand the atmospheric pressure. As a precaution they should always be covered with bagging when in connection with the vacuum system.

CUBAN AMERICAN SUGAR CO.,
NEW YORK and CUBA.

AN IMPROVED PICNOMETER FOR GLYCERIN.

By L. W. BOSART, JR.

Received April 27, 1911.

The picnometer used is of cylindrical form, with thermometer ground in central neck, and with fused-in capillary tube at side.

The Geissler form with ground-in capillary may also be used if preferred.

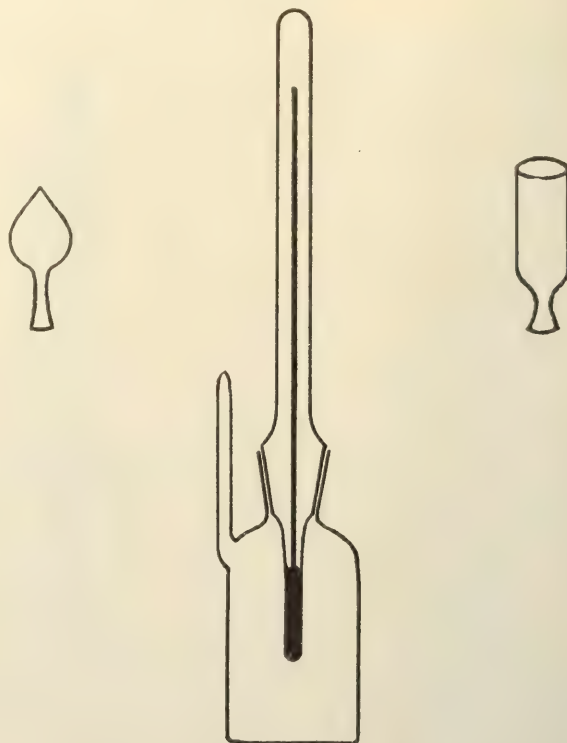
The cap which fits on the capillary tube as usually provided has no opening at the upper end and it is found expedient to attach a rubber tube to the lower opening of the cap, and hold the upper end in the small tip of a blast-lamp flame, while blowing through the rubber tube until a very small hole is blown through the glass.

By means of this hole, the air can escape when the glycerin expands and enters the cap and will not run down the sides of the capillary tube. After the cap has been placed on the apparatus, the picnometer may stand and be weighed at any convenient time.

The improvement on the usual form of picnometer consists of a small cylindrical shaped funnel, 38 millimeters total length, and 15 millimeters outside diameter. This is ground to fit the capillary tube. When the glycerin is poured into the picnometer, this funnel is placed on the capillary tube and filled

with glycerin and the determination can be made irrespective of whether the glycerin at the beginning of the operation is above or below the temperature at which the determination is to be made.

This is found to be much better than placing a rubber tube over the capillary glass tube, as is sometimes



done, as it is easier to see if the funnel is perfectly clean. It also allows for greater contraction of the glycerin and gives opportunity for better observations.

A cover made from the closed end of a test tube may be placed over the funnel to prevent any water being splashed in while the apparatus is in the bath.

Funnels of this description are made for us by Eimer & Amend, to fit the picnometers we had in use.

LABORATORY OF THE PROCTOR AND GAMBLE
MANUFACTURING CO.
NEW YORK CITY.

ADDRESSES.

FACTORY SANITATION AND EFFICIENCY.¹

By C. E.-A. WINSLOW, Associate Professor of Biology, College of the City of New York and Curator of Public Health, American Museum of Natural History, New York.

It may fairly be maintained that in most industries the largest element invested is what may be called life capital. For example, in the cotton industry in 1905 there was invested a capital of 613 million dollars while the pay-roll amounted to 96 million a year. Capitalized at 5 per cent., this pay-roll would correspond to an investment of 1920 million dollars in the form of the hands and brains of the workers. The

¹ Presented before the Congress of Technology, Massachusetts Institute of Technology, Boston, April 11, 1911.

calculation is perhaps a fanciful one; but it illustrates the fundamental fact that the human element in industry is of large practical importance.

Once the operative is trained and at work it is generally assumed that the results obtained will depend only on his intrinsic qualities of intelligence and skill. The effect of the environment upon him is commonly ignored, but its practical importance is very great. In industries where it has been shown that the machine which makes a given fabric requires certain conditions of temperature and moisture for its successful operation these conditions are maintained with exemplary care. In every factory, however,

there is another type of machine, the living machine, which is extraordinarily responsive to slight changes in the conditions which surround it. These conditions, in this relation, we habitually neglect.

I am not dealing now with the sociological and humanitarian aspects of the case. I am quite frankly and coldly, for the moment, treating the operative as a factor in production whose efficiency should be raised to the highest pitch, for his own sake, for that of his employer and for the welfare of the community at large.

The intimate relation between the conditions which surround the living machine and its efficiency is matter of common experience with us all. Contrast your feeling and your effectiveness on a close, hot, muggy day in August and on a cool, brisk, bright October morning. Many a factory operative is kept at the August level by an August atmosphere all through the winter months. He works listlessly, he half accomplishes his task, he breaks and wastes the property and the material entrusted to his care. If he works by the day the loss to the employer is direct; if he works by the piece the burden of interest on extra machinery has just as truly to be borne. At the close of the day the operative passes from an overcrowded, overheated workroom into the chill night air. His vitality lowered by the atmosphere in which he has lived, he falls a prey to minor illness, cold and grip and the disturbing effect of absences is added to inefficiency. Back of it all lurks tuberculosis, the great social and industrial disease which lays its heavy death tax upon the whole community after the industry has borne its more direct penalty of subnormal vitality and actual illness.

The remedy for all this is not simply ventilation in the ordinary sense in which we have come to understand the term. Mr. R. W. Gilbert, of the Massachusetts Institute of Technology, begins a suggestive paper on "The Economics of Factory Ventilation" in *The Engineering Magazine* for December last as follows: "Webster's definition of the word ventilation is 'to air' or 'to replace foul air by fresh.' In actual practice, however, ventilation should mean more than this. It should mean the conditioning of the air of any enclosed space to the best requirements of the occupants of that space." Conditioning of the air so that the human machine may work under the most favorable conditions—this is one of the chief elements of industrial efficiency as it is of individual health and happiness.

The chief factors in air conditioning for the living machine, the factors which in most cases far outweigh all others put together, are the temperature and humidity of the air. In many a plant money has been spent for an elaborate system of ventilation and if the air has been too hot or too dry or too moist the effect on comfort and efficiency has been worse than *nil*. It is a curious instance of the way in which we neglect the obvious practical things and attend to remote and theoretical ones, that for years more attention has been bestowed on the testing of air for carbon dioxide which was supposed to indicate some mysterious

danger than on the actual concrete effect of overheating. Heat, and particularly heat combined with excessive humidity, is the one condition in air that has been proved beyond a doubt to be universally a cause of discomfort, inefficiency and disease. Flugge and his pupils in Germany and Haldane in England¹ have shown that when the temperature rises to 80° with moderate humidity or much above 70° with high humidity, depression, headache, dizziness and the other symptoms associated with badly ventilated rooms begin to manifest themselves. At 78° with saturated air Haldane found that the temperature of the body itself began to rise. The wonderful heat-regulating mechanism which enables us to adjust ourselves to our environment had broken down and an actual state of fever had set in. Overheating and excess of moisture is the very worst condition existing in the atmosphere and the very commonest.

The importance of the chemical impurities in the air has dwindled rapidly with the investigation of recent years. The common index of vitiation due either to human beings or to lighting and heating appliances is carbon dioxide; but carbon dioxide in itself has no harmful effects in tenfold the concentration it ever reaches in ordinary factory air. Nor is there any reduction of oxygen which has any physiological significance. In the Black Hole of Calcutta and below the battened down hatches of the ship *London-derry* there was actual suffocation due to oxygen starvation; but this can never occur under normal conditions of habitation. It was long believed that the carbon dioxide was an index of some subtle and mysterious "crowd poison" or "morbific matter." All attempts to prove the existence of such poisons have incontinently failed. There are very perceptible odors in an ill-ventilated room, due to decomposing organic matter on the bodies, in the mouths, and on the clothes of the occupants. These odors may exert an unfavorable psychical effect upon the sensitively organized but as a rule they are not noticed by those in the room but by those who enter it from a fresher atmosphere. Careful laboratory experiments have quite failed to demonstrate any unfavorable effects from rebreathed air if the surrounding temperature is kept at a proper level. In exhaustive experiment by Benedict and Milner,² 17 different subjects were kept for periods varying from three hours to thirteen days in a small chamber with a capacity of 197.6 cubic feet in which the air was changed only slowly while the temperature was kept down from outside. The amount of carbon dioxide was usually over 35 parts (or eight to nine times the normal) and during the day when the subject was active it was over 100 parts and at one time it reached 231 parts. Yet there was no perceptible injurious effect.

The main point in air conditioning is then the maintenance of a low temperature and of a humidity not too excessive. For maximum efficiency the temperature should never pass 70° F. and the humidity

¹ The literature on this subject is well summarized with reference to original sources by T. R. Crowder in "A Study of the Ventilation of Sleeping Cars," *Archives of Internal Medicine*, 7, 85

² Bull. 136. Office of Experiment Station, U. S. Dept. of Agriculture.

should not be above 70 per cent. of saturation. At the same time a too low humidity should also be avoided. We have little exact information upon this point but it is a matter of common knowledge with many persons that very dry air, especially at 70° or over, is excessively stimulating and produces nervousness and discomfort. It would probably be desirable to keep the relative humidity between 60 and 70 per cent.

Another point which may be emphasized in the light of current opinion is the importance of "perflation" or the flushing out of a room at intervals, with vigorous drafts of fresh cool air. Where there are no air currents the hot, moist vitiated air from the body clings round us like an aerial blanket, as Professor Sedwick calls it, and such of us is surrounded by a zone of concentrated discomfort. The delightful sensation of walking or riding against a wind is largely perhaps due to the dispersion of this foul envelope and it is important that a fresh blast of air should sometimes blow over the body to produce a similar effect. The same process will scatter the odors which have been noted as unpleasant and to some persons potentially injurious. The principal value of the carbon dioxide test to-day lies in the fact that under ordinary conditions high carbon dioxide indicates that there are no air currents changing the atmosphere about the bodies of the occupants.

There is one other problem of atmospheric pollution to which special reference should be made. The presence of noxious fumes and still more the presence of fine inorganic or organic dust in the air constitutes a grave menace to health in many processes and is an important contributory cause of tuberculosis. The normal body has its "fighting edge" and can protect itself against the tubercle bacillus if given a fair chance, but the lung tissue which is lacerated by sharp particles of granite or steel quickly succumbs to the bacterial invader. In dusty trades like stone-cutting and cutlery working and emery-grinding, 75 per cent. of all deaths among the operatives are due to tuberculosis, against 25 per cent. for the normal adult population. This may be fairly interpreted as meaning that the actual death-rate from tuberculosis in these trades is from two to four times as high as in a corresponding average population; in other words, 3 or 4 or 5 out of a thousand of these workers are sacrificed every year to the conditions under which they labor. The elimination of the dust by special hoods and fans is imperative in such industries and must be supplemented in extreme cases by the compulsory use of respirators.

It is extraordinary how little is known to-day of the actual conditions of factory air, either by manufacturers or by sanitarians. So far as I am aware the New York Department of Labor is the only state department dealing with factory inspection which collects and publishes exact data in regard to the quality of the atmosphere in the workshops. If the conditions indicated in these reports by Mr. C. T. Graham Rogers are typical, and there is no reason to doubt that they are for the smaller industries at least,

there is urgent need for betterment. The table below shows that of 215 workrooms inspected 156 or 73 per cent. had a temperature of over 72°, and 63 or 29 per cent. exceeded 79°. In tabulating these analyses I have excluded all cases where the outdoor temperature was over 70°.

TEMPERATURE AND HUMIDITY IN NEW YORK FACTORIES.

Industry.	Number of work-rooms with temperature.			Relative humidity.
	72° or less.	73°-79°.	80° or over.	
Printing.....	2	25	29	3
Clothing trades.....	9	23	7	6
Bakeries.....	1	20	15	7
Pearl button mfg.....	33	9	0	14
Cigar-making.....	8	4	5	7
Laundries.....	0	7	7	1
Miscellaneous.....	6	5	0	1
Total.....	59	93	63	39

In Massachusetts quantitative data of this kind are lacking, but the general results of inspection by the State Board of Health indicate similar conditions. In the report on the sanitary conditions of factories and workshop made by the Massachusetts State Board of Health in 1907, is the following comment upon the boot and shoe factory:

"In the majority of factories visited, the ventilation was found to be poor, and in many of them distinctly bad. Of the rooms not especially dusty, 102 were badly ventilated and 26 were overcrowded. In the rooms in which large amounts of dusts are evolved, the number of machines with means for efficient or fairly efficient removal of dust was found to be 1630; the number either inefficiently equipped or devoid of equipment was 2769.

"Of 84 of the many dusty rooms reported, 40 were also overcrowded, 35 were dark, 21 overheated, and 18 were overcrowded, dark and overheated. In more than one-third of the factories visited, the conditions of water-closets were not commendable; most of them were dark and dirty to very dirty."

There is plenty of evidence, though of a scattered and ill-digested sort, that the elimination of such conditions as these brings a direct return in increased efficiency of production. The classic case of the U. S. Pension Bureau is always quoted in this connection. The removal of the offices of the department from scattered and poorly ventilated buildings to new and well-ventilated quarters reduced the number of days of absence due to illness from 18,736, which figure it had been for several successive years, to 10,114.

In an investigation of my own of conditions in the operating room of the New England Telephone and Telegraph Co., at Cambridge, Mass., I found that before the installation of a ventilating system, 4.9 per cent. of the force (150-60 girls) were absent during the winter months of 1906 and 4.5 per cent. in 1907. The ventilating dust which was put in was a simple one and cost only about \$75.00 to instal but in the winter of 1908 following its introduction the absences were cut down to 1.9 per cent. of the force employed, without any other change in conditions or personell so far as I was able to discover.

¹ Report of the Commissioner of Labor for 1908, 1909 and 1910.

Mr. Kimball cites a number of similar cases in a paper on "Ventilation and Public Health" published in *The Annals of the American Academy of Political and Social Science* for March, 1911, the most striking of which are as follows:

"The Germania Insurance Company of New York in 1910 had eighty clerks in one office. Previous to the proper ventilation thereof, 10 per cent. were absent on account of illness all the while. Since then the absenteeism has been reduced to nothing.

"The vice-president of the Manhattan Trust Company of New York states that by proper ventilation he has so increased the efficiency of his clerical force that he has been able to reduce the number of employees 4 per cent.

"In a printing establishment in New York, a ventilation system was installed because of the insistence of the State Department of Labor that the law be complied with, the order having been resisted for two years. After the system had been in use a year the proprietor stated that had he known in advance of the results to be obtained no order would have been necessary to have brought about the installation. Whereas formerly the men had left work on busy days in an exhausted condition and sickness was common, now the men left work on all days in an entirely different condition, and sickness had been much reduced. The errors in typesetting and time required for making corrections were greatly reduced.

"Townsend, Grace & Company, of Baltimore, built a straw hat factory without ventilating apparatus. The first two winters after occupation the sick-rate was 27½ per cent. A ventilating system was then installed after which the winter sick-rate fell to 7 per cent. It was claimed that the ventilating system paid for itself in one year."

It is much to be desired that this problem should be studied by careful quantitative methods as a definite factor in the profit and loss account. The National Electric Lamp Association is approaching the question of sanitary conditions in this manner, comparing in detail the temperature and humidity of its work-rooms with the hours of work, the pay and the efficiency of its employees. Only by such systematic study can it be determined how much factory sanitation is really worth in any given case. The evidence is already strong enough, however, to warrant some investigation. In cases where preliminary study shows its value, why should not the sanitary inspection of a factory be made a part of its operation just as supervision of its mechanical features is a part of its organization to-day? It is not solely or chiefly the problems of ventilation as ordinarily understood that should be studied; and it must be remembered that there is never anything magical in a "ventilating system." "Systems" are as dangerous in sanitation as quackery in medicine. The problem must be approached from a broad biological viewpoint, and should include all the conditions which make for lowered vitality. Temperature and humidity come first and foremost, and dust and fumes must be guarded against in certain processes. The cleanliness of the factory, the purity

of drinking water, the quality of lighting, the sanitary provisions and a dozen other points will suggest themselves to the skilled investigator when on the ground. He may find in many of these directions economic methods by which efficiency can be promoted.

The consulting factory sanitarian will be a new factor in industry but the progress of industrial economy and of sanitary science unite in pointing to the need for such an expert. If the manufacturers will fully utilize the resources of technology in this direction they can write a new chapter in the history of industrial efficiency.

REVIEW OF ELECTROCHEMICAL DEVELOPMENT.¹

By E. A. SPERRY

Received April 24, 1911

The fundamental factor in bringing about the era in which we live, the great factor which characterizes the present day and distinguishes it from ancient times, is the application of power. Authorities, the world over, agree to this. It is often stated as being the "introduction of machinery." But there would be little machinery without ready, cheap and practical sources of power.

In reviewing the early products in the various lines of activity, we are often struck with the wonderful ability exhibited in ancient times in the various branches; for instance, oratory and statesmanship were probably carried to as high a point as anything we can exhibit in modern times. We are also familiar with many examples of art and architecture produced in these early times, which equal, if not excel, examples of the present day, and even in matters relating to engineering; bridges and aqueducts were constructed, evincing wonderful knowledge in fundamentals. In many cases their dexterity excelled our own execution, for we must remember that an endless variety of implements, which to us are perfectly familiar and in every day use, were totally unknown to these early workers. In the realm of power, however, and its myriad applications, we have what probably constitutes the greatest single advance of modern times.

I do not think that any one will hesitate in agreeing also that this especial epoch, in the dawn of which we now live, is likely to be known as the age of electricity. It has fallen to my lot to be more or less intimately acquainted with the phenomenal and wonderful advances in this field, advance taken by *leaps* and *bounds*; in single decades advances have been made equal to whole centuries in many other lines of activity.

In the spring of 1884 I became the only Western delegate to come to this city from Chicago, to help in organizing the American Institute of Electrical Engineers. A small group of us gathered in the modest rented quarters of the then young society of Mechanical Engineers, on 23rd Street, and I became the fifth to sign the charter and placed my money on the table in the original act of organization of that society. A

¹ Address before the annual meeting of the American Electrochemical Society, New York, April 7, 1911

small group of earnest men builded wiser than they knew in thus organizing a society which has since become a body of international importance, and one doing much in the direct advancement of science and art in this important field, with its myriad branches and avenues of activity. Its members now number upwards of seven thousand.

It must be remembered that at this time the only practical and commercial application of electricity was in lighting. In the Spring of the next year it so happened that I was Chairman of the Committee of Call of the first Convention of the National Electric Light Association, which we organized in the City of Chicago in 1885, and which is now a flourishing organization, having some eight thousand members doing a vast work in many fields of practical application of electricity, especially leading in the work of conversion of all natural sources of power throughout this country.

The topics and subjects brought up for discussion at this first Convention would have amused, if not amazed, this present audience. Earnest questions as to the possibility of being able to use electricity as a motive power, and recounting disastrous results in trying to use the few small electric motors of the time, all give a vivid idea of the struggles and discouragements of those pioneer days.

The art and industry which we foster represents the most direct and most recent development of this great advance movement in the application of power, in that we bring power or energy in its most controllable, as well as its most active form, name *electricity* to bear upon chemical actions and reactions, resulting in many fields, in a much more direct and economical solution of the problems involved; in numerous instances, in products otherwise unattainable and working economies which at once place valuable elements and compounds within reach of all, thus rendering great service to mankind.

Electrochemistry as such may be said to be largely American in its origin, and emphatically American in its practical development. I speak advisedly on this point. Our great water power resource and development are not alone responsible for this, the enterprise and enthusiasm of our technical and commercial men have played no small part in this great work. Such names as those of Castner, Hall, Wilson, Atcheson, Herreshoff, Townsend, Dowe, and a host of others testify to this. As to this art being American in its large practical development, one has only to recount the numerous chemical processes we have imported bodily from Europe, and almost without change adopted. Outside of this long list it should be remembered that we are still currently importing a large amount of chemical products. The contrast with this quite strikingly emphasizes the point we make that in the field of electrochemistry we have been enabled to very largely supply the entire demand for electrochemical products and cut down very materially, if not entirely, importation.

The value of the electrochemical, as compared with

the purely chemical method, is illustrated by the "Solvay" process which was imported from Belgium and which employs as its principal raw material, sodium chlorid, or common salt; but in the operation of this process only one of the elements of this valuable compound, namely the sodium, is recovered. Our State was recently called upon to condemn and to relinquish a lake of quite considerable size, for receiving the deposit containing the other element, namely chlorin, which is a waste product rejected in this process. In a number of electrolytic plants in this country where the same raw material is employed, practically 100 per cent. of both of these constituent elements are recovered and rendered available and useful, certainly marking an advanced movement in the point of conservation of our mineral resources. This illustrates one only of the advantages following the direct application of electricity in processes that are known as "electrolytic." Our good Mr. Herreshoff here present tells me that practically 90 per cent. of all the copper that is used in the world is refined electrolytically. Seventy or 80 per cent. of the original copper contains arsenic, minute quantities of which are known to degrade copper and render it practically useless as an electrical conductor. The electric arts employ about 70 per cent. of all the copper produced; thus the circuit may be said to be closed in two ways—the electrolytic ministering to the electrical.

There is quite a dramatic aspect connected with this electrolytic copper refining not popularly understood. Think of nine hundred thousand tons of this beautiful, glistening, red massive metal existing as a perfectly clear, watery solution in one stage of its life history, during its transit from anode to cathode after it has been dissolved by the direct action of electrical energy in the electrolyte!

Started in Germany, this process was taken up actively in England, but now it may be said that America is its home; certainly, by far, its greatest activity is to be found here, and we have here present probably the greatest worker in this art; certainly the one who has brought to its highest perfection electrolytic copper refining.

Again, electrolysis has given the world aluminum. Only a few years ago this metal was \$6.00 a pound. Then it gradually came down to \$1.00. The engineering world then gave its use the first passing thought. Hall in this country and Heroult abroad, working on and on, through many discouragements, succeeded finally by its electrolytic production; by the direct application that this method affords, in supplying the energy for which this element has an enormous appetite, and so reducing its cost as to place it within reach of all. In consequence, its industrial applications have broadened, until 50,000 tons, valued at \$20,000,000, are annually consumed. This metal also, like the copper, is in the form of a perfectly clear solution in one stage of its life history, with this difference, however: that in the case of the copper, the solution stage constitutes what may be termed its "graduation certificate," whereas with

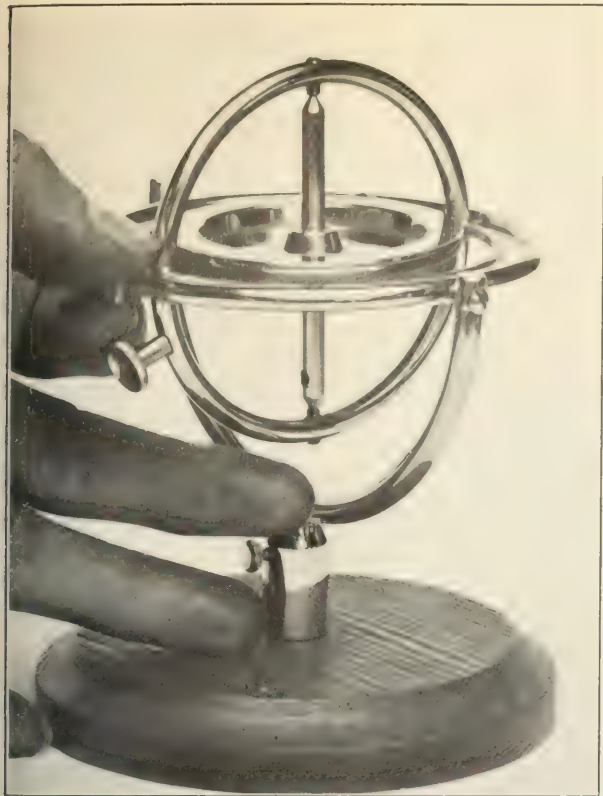


Fig. 1.



Fig. 2.



Fig. 3.



aluminum, it is even more far-reaching and actually constitutes its "birth certificate."

I might go on numerating interesting examples of these direct applications of electricity for producing chemical reaction, both in electrochemical and thermal applications which constitute the principal activities and interests of our members. For instance, a most valuable product, calcium carbide, would not exist were it not for the electric furnace, this process having been discovered and brought out in this country by Mr. Wilson.

One fact which arrested my attention, however, and for which I crave your indulgence for a moment more, is a fact brought out recently by the noted authority in the field of original research, the next speaker, Dr. Whitney, of Schenectady, when he stated that it was a fortunate circumstance when bodies were energized or otherwise induced to react, they did not directly tend, in the majority of cases, to reproduce the energy, or energy of the same form; for instance, reactions do not tend directly to produce heat, but, on the contrary, when energy, such as heat or electricity, is applied and a reaction takes place, a new compound is produced, that is, the operation "side-steps," so to speak, bringing about a new, and, broadly speaking, an unexpected result. This phenomena of indirection, as it may be called, seems to me to be a general law, a sort of a by-pass which nature takes in producing variety.

It may be stated that this is the manner in which variety occurs. So universal is this method that, as a matter of fact, it is difficult to obtain a reaction which *does* give back the energy in the same form as applied, *e. g.*, the delicate processes necessary in constituting what is known as the storage battery, whereby electricity may be again returned after first having been introduced.

The universal law seems to be one of translation instead of oscillation. In fact, upon introduction, stresses will give you almost anything except a return of the particular stress, qualitatively. This phenomena having such a very striking and complete homologue in a totally different branch of science and one to which I have devoted considerable attention, I may be pardoned if I bring it to your attention by the use of a model which serves to illustrate in a most vivid way just what I mean. I hold before you a gyroscope having Cardan or universal mountings. The outer ring being pivoted, I now swing it back and forth, and we see the inner ring which is mounted therein and its wheel simply partake of the same motion, and that nothing whatever peculiar occurs, that is, all of the parts move together, just as they should, back and forth, upon the pivots of the outer ring. But suppose I now spin up the wheel within its inner ring and repeat the same operation, that is, attempt to swing the outer ring to and fro upon its pivots as before. Our attention is at once arrested by the very peculiar, vigorous and unexpected motion which the inner ring now makes. It is

evident that this motion is not only automatic, being self-developed, but it seems to bear no relation whatever in this direction to that of the impressed forces, and upon close examination we find that it exists to the normal, or actually at right angles to the line of the original energization. As a matter of fact, it "side-steps," and this it does invariably. With each application of stress in a given line or plane, the inner ring moves to and fro in a plane at right angles, "side-stepping," so to speak, under the impressed stress, and in a line or direction just as far removed from that of the impressed forces as it is possible for it to do, namely 90° measured either uniplaner or as a spherical function. Here we have this phenomenon in a form which we can handle, study, weigh and measure. The homologue, I believe, has a very far-reaching significance and one which I cannot but believe derives its fundamental activity in this devious path from the same underlying principle, namely *rotation*. It need not be rotation about its own axis, as in the case of the inner wheel before us, but it may be rotation about a remote center of which the observer has no knowledge, nor the existence of which he even suspects, yet all that is required is the presence of rotation or angular velocity, and when this is present in either ion, atom, molecule or mass, there invariably exists a definite and powerful tendency; a definite ponderable moment of effort in this new direction to one side practically at right angles to that of the stress or forces impressed. These phenomena are not only qualitatively analogous, but I believe them to be quantitative and determinable.

Nor should we look upon such a solution of this action which seems almost universal, as less significant. When we remember that motion itself is universal, all nature seems to be either in a state of motion or consisting of motion in its deeper significance.

As the underlying principles of these motions are better understood, why should we not be able to assign definite values, to pre-cast definite directions in which the movements or reactions should proceed, and with the same degree of precision that we are now enabled to apply in that branch of the useful arts in which this self-same phenomenon is fundamental, is just now in rapid state of development and is destined to become an extremely important and useful force in the service of mankind?

I hope that this seeming digression may be pardoned. By the use of the model I have endeavored to make clear to you the true nature of this phenomenon; the strange, physical reaction which we know as gyroscopic precession. Knowledge of this action was made use of by our great contemporary, Sir J. J. Thompson, in a number of notable observations made not long since, and I am hoping that it may so impress itself upon your minds as to be equally useful to you. It should not be understood that the observations and statements I have made are put forward as being in any way final, but are intended to be more in the line of suggestion.

THE CHEMIST IN THE SERVICE OF THE RAILROAD.¹

By H. E. SMITH.

Received April 20, 1911.

Among the industries of the country, the railroads are probably the largest, whether they be judged from the standpoint of investment required, territory covered, or men employed. Considered as manufacturing establishments, the railroads use as raw materials, iron and steel of all kinds, brass, bronze and babbitt, wood and timber of all kinds, stone, brick, cement, oils and paints, and a great number of materials of lesser importance. The manufacturing process covers various departments of field engineering, power production, shop work and metallurgy. The finished product is the transportation of passengers and freight.

As in numerous other manufacturing industries, the equipment required is constantly becoming heavier, more elaborate and expensive. The methods of operation are constantly becoming more complicated, more specialized and more costly, yet the piece price of the product, transportation, is constantly diminishing.

This condition evidently necessitates increasingly scientific management and operation. The need of the civil, the mechanical and the electrical engineer is obvious. With the increasing development has come the need of the chemist and, beginning nearly thirty years ago, the Massachusetts Institute of Technology has at various times furnished chemists for this service.

As has already been partially indicated, the field for the chemist in railroad service is very wide. Early in the construction of a first-class road the chemist is in demand for the testing of cement, to ensure sound and durable concrete bridges and other structures; in the selection of ballast stone of such composition and physical properties that it will withstand the weather and the impact and wear of service. Timber for cross ties now commands such a price that economy necessitates preservative treatment by carefully tested and regulated materials and processes. Rails must be of such composition that they will resist wear in the greatest possible degree, yet be free from brittleness.

The problem of boiler water supply, especially that for locomotives, is of very great importance. An average modern locomotive is a complete power plant of 2000 horse power, mounted on wheels, and contained within a space only a fraction of that required by a stationary power plant of the same capacity. About one hundred gallons of water are evaporated per mile traveled. In many parts of the country the only water available is of such quality that economy in operation requires its chemical purification. This brings to the chemist the problem of carrying out chemical reactions on a large scale, and in extremely dilute solutions, yet with very close adjustment and at low cost.

Iron castings are used in such quantities that railroad companies frequently make their own. The

pig iron and the coke must be tested to ensure proper quality. The mixtures must be adjusted to secure the necessary product. Car wheels must be tough and strong yet very hard on the circumference, to resist wear. Machinery castings must be strong yet machine easily. Packing rings must be very resilient. Yet in all mixtures economy must be practiced by using up scrap.

The proper selection of steel for efficient and economical service is a constant problem. Special alloy steels, either with or without special heat treatment or other manipulation, are used in increasing quantities. It is necessary to make very frequent and systematic chemical and physical tests to ensure uniform and satisfactory quality.

Large quantities of brass or bronze, mostly in the form of bearing metal, also babbitt for the same purpose, are required. The prices of the constituent metals vary from five to thirty-five cents per pound, which constitutes a strong temptation to substitute the cheaper for the more expensive, so far as possible. The chemist must be called upon to detect such substitution and to determine whether the constituents have been properly proportioned. Scrap must be utilized and the chemist is needed to test the remelted metal and adjust its composition to standard figures.

Paints are used in large quantities on cars, buildings, bridges, etc. The pigments are frequently adulterated with inferior, inert or injurious minerals, the linseed oil with petroleum and inferior vegetable oils, and the turpentine with benzine. The proportions of the specified ingredients must also be checked. Lubricating and burning oils constitute another important class of material for study, to secure the proper selection of grades and maintenance of satisfactory standards.

The list of articles which come up for occasional attention includes soaps, greases, roofing materials, fireproofing materials, various chemicals, minerals and ores, rubber, battery materials, dyestuffs, inks, grinding and polishing materials, disinfectants, rope, cotton and woolen waste, fuel, etc.

Not only must all these materials be examined after purchase, but many of them must be bought on definite specifications in order to secure the desired quality under competitive bids. The writing of the specifications falls chiefly upon the chemist. To this end he must study carefully the needs of the service, the quality of material best adapted to meet those needs, as well as the quality available on the market and finally the methods of test best adapted to determine the quality. This exhaustive study may also be the means of ultimately developing or improving various industries so that it is beneficial not only to the consumer but to the producer.

It is natural that the chemist should also be required to study various methods and processes of operation in different parts of the railway service with a view to the economy of material or labor or to increasing the efficiency of the service.

In all the work above described, the investigator must be more than a chemist. He must be some

¹ Read before the Congress of Technology, Massachusetts Institute of Technology, Boston, April 11, 1911.

thing of a geologist, a physicist, a metallurgist, an electrician or a sanitarian, as the case requires, and withal must have the ability to predict the effect from the cause, or to trace back from the effect to the cause.

It is for these reasons that the broad and comprehensive training offered by the Institute of Technology is especially adapted to fit men to take up scientific work for the modern railway.

SCIENTIFIC SOCIETIES

SOCIETY OF CHEMICAL INDUSTRY.

Annual general meeting to be held in Sheffield, England, July 12-13-14, 1911.

PROGRAM.

WEDNESDAY, JULY 12TH.

Morning.

10 A.M. Council Meeting at the Cutlers' Hall.

10.30 A.M. Annual General Meeting and Address by the President.

1 P.M. Luncheon at the Grand Hotel, Leopold Street, by invitation of the Yorkshire Section.

Afternoon.

Visits to the following works:

- (a) Peter Dixon & Son, Paper Mills, Oughtibridge.
- (b) The Sheffield Simplex Motor Works, Tinsley.
- (c) James Dixon & Son, Cutlery and Silver Works, Cornish Place.
- (d) Tennant Brothers, Ltd., Brewery.
- (e) W. S. Laycock's Railway Carriage, Steamship, and Tramcar Fittings Works, Millhouses.
- (f) Thomas Firth & Sons, Norfolk Steel Works, Savile Street, East.

Evening.

Annual Dinner at the Grand Hotel, Leopold Street, at 7.15 for 7.30. Tickets, excluding wine, 7 s. 6 d.

THURSDAY, JULY 13TH.

Excursion.

Newton Chambers & Co., Thorncliffe, and the Wharnccliffe Silkstone Colliery, Tankersley.

Including:

- (a) Koppers Retort Ovens and By-Product Plant.
- (b) Manufacture of Izal Disinfectant.
- (c) Demonstration of Life-saving Appliances in an Irrespirable Atmosphere at the Rescue Station.
- (d) Simon-Carves By-Product Coke Ovens and Utilization of Surplus Gas for Power Purposes.

Messrs. Newton Chambers & Co. will provide lunch. Return tickets 1/6 each.

EXCURSIONS.

Morning.

- (a) The Grimesthorpe Works of the Sheffield United Gas Light Co.
- (b) John Brown & Co., Atlas Steel and Iron Works.
- (c) William Cooke & Co., Ltd., Tinsley Steel, Iron, and Wire Rope Works.
- (d) William Hutton & Sons, Cutlery and Plate Works, West Street.

(e) Mappin & Webb's Cutlery and Silver Works, Norfolk Street.

(f) The Metallurgical Department of the University of Sheffield, St. George's Square.

Afternoon.

(a) Cammell Laird & Co's. Grimesthorpe Steel and Iron Works.

(b) Vicker's River Don Steel Works.

(c) Park Gate Iron and Steel Works, Rotherham.

(d) Steel, Peech, & Tozer's Phoenix Special Steel Works, The Ickles.

(e) Joseph Rogers & Sons Cutlery and Silver Plate Works, Norfolk Street.

(f) Walker & Hall's Cutlery and Silver Plate Works, Howard Street.

Evening.

Reception by the Lord Mayor and Lady Mayoress at the Town Hall at 8.30 P.M.

FRIDAY, JULY 14TH.

Excursion.

Drive over the Derbyshire Moors, visit to Chatsworth House and Grounds, and Haddon Hall, returning by Bakewell. Inclusive tickets 12/6 each.

Evening.

9 P.M. Smoking Concert at the Grand Hotel.

A detailed program with request form will be issued with the June 15th number of the Journal.

Ladies are invited to all the fixtures.

All communications should be addressed to the Secretaries, 67 Surrey Street, Sheffield.

THE PITTSBURG MEETING OF THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS.

The meeting was an unusually important and successful one, both with respect to the attendance—some 600 members and guests being registered—and the value and interest of the papers considered at the technical sessions.

Three afternoons were devoted to excursions to various industrial plants in the vicinity of Pittsburg.

The meeting was opened on Tuesday evening with an informal reception of the visitors in the Schenley parlors, at which one notable event was the presentation to the President of the Society, Col. E. D. Meier, of an engrossed testimonial expressing the high regard of the members of the Society for Col. Meier's professional attainments and personal character. The presentation was made appropriate by the fact that the day was Col. Meier's 70th birthday. Those joining in presenting this testimonial to Col. Meier have arranged to have his portrait painted.

The regular work of the convention began on Wednesday morning with the semi-annual business meeting. The only matter of particular interest taken up at this meeting was the report of a committee which presented a schedule of standard dimensions for flange pipe fittings of all sizes, from 1 $\frac{1}{4}$ inches to 24 inches, both for standard weight pipe and extra heavy pipe. These standards were prepared jointly by a committee of the National Association of Master Steam and Hot Water Fitters and a committee of the American Society of Mechanical Engineers. The standards will be printed and made available for those interested.

The Society is inaugurating a new departure in an endeavor to adequately cover a number of specialized fields of work, in which the mechanical engineer's work has become of great importance. Through the Society's Meetings Committee, special committees are being organized, each one of them having responsibility for a certain particular branch of mechanical engineering. The engineering of cement manufacture is one of these branches, and the morning was spent in consideration of a number of papers relating to this field.

NATIONAL ELECTRIC LIGHT ASSOCIATION.

The thirty-fourth convention of the National Electric Light Association, which was held at the Engineering Societies' Building, New York, from May 29th to June 2nd, inclusive, broke all records for attendance, over 5,000 members and guests being registered. The meeting was made up of 16 sessions, divided between general, commercial, technical, accounting and power transmission, three parallel sessions being the rule. Numerically the commercial section sessions were the most attractive to the delegates, and although the smallest of the halls was allotted to the accounting sessions, this was not true of the attendance. In addition to the regular chapters a meeting of the Public Policy Committee was held at the New Theater, and there Mr. Samuel Insull read the set report of the committee, which concerned the various forms of welfare-co-partnership and insurance work among employees. This was followed by an address by Hon. Charles Nagle, Secretary of Commerce and Labor, who lauded the proposals of the committee, claiming that the adoption of them would go a long way toward warding off unwise legislation.

PHARMACOPOEIA TRUSTEES.

The first annual meeting of the Board of Trustees of the United States Pharmacopoeial Convention for the term of 1910-'11 was held at Philadelphia on May 5th and 6th, with the full board in attendance. Prof. James H. Beal, of Pittsburg, was elected chairman, and Dr. Henry M. Whelply, of St. Louis, secretary. The accounts of the treasurer showed that he had received a balance of \$8,394 from his predecessor, the treasurer from 1900-1910. The sales of the English edition for the fiscal year ending April 30, 1911, amounted to \$6,188 and of the Spanish edition to \$1,169. Two hundred and ninety dollars were received as royalty from the use of the text and \$172 as interest, making the total receipts \$16,213. The total expenditures, including the expenses for the convention of 1910, amounted to \$7,874, leaving a cash balance on hand of \$8,339.

INTERNATIONAL AGRICULTURAL CONGRESS.

The International Agricultural Congress has decided that the tenth Congress shall take place in Belgium in 1913. A preliminary meeting will be held in Paris next year.

The Rumford Prize of the American Academy of Arts and Sciences was awarded to Prof. J. M. Crafts for his studies in high temperature thermometry at the recent annual meeting of the Academy.

Prof. Jacques Loeb, of the Rockefeller Institute, has been elected a correspondent of the Academy of Natural Sciences of Philadelphia.

The fourteenth annual meeting of the American Society for Testing Materials was held in Atlantic City June 27th to July 1st.

The annual meeting of the National Commercial Gas Association will be held on October 23, 1911, in Denver Colo.

The International Acetylene Association will hold its annual meeting in August, 1911.

EDUCATIONAL

SPECIAL COURSE IN HIGHWAY ENGINEERING.

The Trustees of Columbia University announced at their June meeting the establishment of a new course of instruction in Highway Engineering and have called Arthur H. Blanchard, of Brown University, as Professor of Highway Engineering.

The establishment of this course is due to the widespread interest in the cause of good roads and the

need of a closer scientific study of the various problems involved in road materials and construction. It is believed that systematic instruction in the fundamental principles of highway engineering will lead to standardization and improvement.

The success of this course in Highway Engineering has been insured by the gift of \$10,000 annually for five years from Mr. Charles H. Davis, C.E., '87.

EUROPEAN SCHOOL STATISTICS.

Consul General T. St. John Gaffney reports that there are 465,451 schools with 45,500,000 pupils in Europe, presided over by 1,119,413 teachers. According to the average, there is 1 teacher to every 45 scholars. Twelve years ago there was only 1 teacher for every 60 scholars. The number of teachers in Russia is about 195,000, while those in Germany number 168,000. In Russia there is 1 teacher to every 644 inhabitants, and in Germany there is 1 teacher to 361. In England there are 177,500 teachers occupied, which allows 1 teacher to every 234 inhabitants. In Germany there are 3 illiterates to each 1,000 of population, while in England the reare 10. The most illiterates are to be found in Russia, where there are 617 to every 1,000 inhabitants. In Germany 68 per cent. of the attendance at the schools is composed of children between the ages of 5 and 15; in Russia the average is only 27 per cent.

Mr. T. C. DuPont has given \$500,000 to the Massachusetts Institute of Technology toward its proposed new site. Announcement is also made of a trust fund of between five hundred and six hundred thousand dollars, created by Francis B. Greene some five years ago, for the assistance of students, and \$500,000 from the bequest of Mrs. Emma Rogers, widow of William B. Rogers, the first president of the institute. These large gifts, in addition to the \$100,000 for ten years appropriated by the state, will make it possible for the institute to purchase a new site and erect the necessary buildings.

Governor Foss has signed the bill by which the Massachusetts Institute of Technology will receive \$100,000 annually from the state for ten years. By the terms of the measure the Institute will maintain 80 free scholarships to be apportioned among the 40 senatorial districts of the state.

The H. F. Kieth Company, of Boston, have given \$5,000 to the Massachusetts Institute of Technology, for a research on the decomposition and general

wholesomeness of eggs and for an investigation of the bacterial and chemical content of the product under varying conditions.

Dr. Bertram B. Boltwood, professor of radio-chemistry at Yale University, was elected to membership in the American Philosophical Society at its recent meeting, as was also Dr. A. A. Noyes, professor of physical chemistry at Massachusetts Institute of Technology.

Dr. Theodore William Richards, professor of chemistry at Harvard, who is going to England at the invitation of the Chemical Society to deliver the Faraday lecture, will be given the honorary degree of D Sc. by the University of Manchester on July 8th.

During his presence in New York City Dr. Svante Arrhenius lectured at the College of the City of New York on the afternoon of May 17th, at the Chemists' Club on the evening of May 17th and at Columbia University on May 18th.

Prof. Charles H. Fulton has resigned the presidency of the South Dakota School of Mines, Rapid City, S. D., and is going to the Case School of Applied Science, Cleveland, Ohio, as professor of metallurgy and head of its mining department.

Lieut. Col. W. Robinson, of the U. S. Army, has been nominated by President Taft to be professor of chemistry at West Point commencing October, 1911, to succeed Col. S. E. Tillman who will retire then.

Dr. W. F. Watson, professor of chemistry and biology in Furman University, Greenville, S. C., has resigned the chair which he has occupied since 1890.

Dr. C. F. Mabery, professor of chemistry in the Case School of Applied Science, has resigned the chair which he has held since 1883.

OBITUARIES

NATHANIEL WRIGHT LORD.¹

1854—May 23, 1911.

Nathaniel Wright Lord, born at Cincinnati, Ohio, December 26, 1854, sprang from a notable ancestry. His father was Henry Clark Lord, a man prominent in the business and political life of his time, and son of Nathan Lord, for many years President of Dartmouth College; his mother Eliza Burnet Wright, a woman of rare vigor and ability.

Professor Lord's education was begun in the public schools of his native city, and their training, developed by a year of searching review under an ex-

¹ Memorial adopted by the Faculty of Ohio State University in special session May 24, 1911.

acting foreign tutor of rare gifts, was enlivened by frequent boyish forays into fields of natural history. Hence, the rigorous course in mining engineering taken 1872-76 at Columbia College School of Mines caused him no difficulty. Next came a year of hardship in Central American mining, which nearly cost him his life. Upon his return and recovery the young engineer was appointed, November 6, 1878, State Analyst at Ohio State University. On June 18, 1879, the Department of Mining and Metallurgy was entrusted to him, and remained under his control until the end of his life.

Professor Lord's professional career was largely developed in the service of this institution. His

earliest engineering experience as the chemist and technical director of a Gold Mining Company in Nicaragua, though it had been of great service in developing his power and self-confidence in the application of science to engineering, yet had given him little reputation. In the new position his ability and energy were soon recognized. He became, in 1883, chemist of the Geological Survey of Ohio, contributing in addition to his chemical reports valuable chapters on the iron industry and on the differentiation of the coal seams of the state by novel methods. His grasp of these subjects was so masterly that he became a national authority on fuels and fuel-testing, and for the past eight years has been chief chemist or consulting expert of the Technologic Branch of the United States Geological Survey, now the Bureau of Mines.

Upon the College of Engineering, Professor Lord has left an enduring mark. As its first Dean, beginning in 1896, he carried it through its formative period, and left it with policies and ideals well crystallized. His sane and practical mind rejected instantly everything that savored of show or pretense. As in his engineering, so every educational plan must rest upon a solid foundation. His constant struggle was to ground his students thoroughly—well assured that upon such a foundation they would erect a secure superstructure. His teaching was a constant appeal to the reason, and to the constructive imagination. To see him with a class attack a problem new to both was a rare experience.

Combined with his power and inspiration as a teacher, was his pre-eminent ability as an investigator. The training of the chemical laboratory, where everything must be accounted for, gave to his naturally incisive thinking processes a precision and analytical power most unusual. No man could with more unerring certainty strip a complicated problem of its

disguises and lay bare its fundamental principles. No field of science upon which he touched failed to profit in some enduring way from his ever active mind.

No man could associate with him in any capacity without admiring him; his large mind and generous spirit had no room for anything little or sordid. Creditable, useful, even brilliant, as many of his contributions to science and engineering have been, his influence on his students and on his colleagues is the signal proof of his greatness.

To the very last he was a man of diversified interests and continually entered upon new pursuits with characteristic enthusiasm.

Professor Lord was a man of marked intellectual vigor. His mind was no less judicial than analytical. He thought clearly and spoke with logical precision. In action he was prompt, decided and fearless. His moral convictions rested upon reason rather than upon authority or tradition.

With the reserve of a gentleman who permitted no undue familiarity, he yet remained essentially democratic, and no one felt humbled in his presence. Honesty was fearless before him. To those who won his confidence, he was a loyal friend and a wise counselor.

In the death of Professor Lord this Faculty mourns the loss, not merely of their colleague of longest unbroken service, but of the brilliant man of science, the incisive and powerful teacher, the keen yet broad-minded counsellor, the vigilant and strong supporter of the university, the loyal citizen, delightful companion and generous friend, the man of rare quality, originality and broad interest, whose place in the hearts of those who knew him intimately, can never be filled.

S. C. DERBY,
WILLIAM R. LAZENBY,
EDWARD ORTON, JR.

NOTES AND CORRESPONDENCE.

CONDENSATION PRODUCTS OF PHENOLS AND FORMALDEHYDE.

To the Editor of the Journal of Industrial and Engineering Chemistry.

SIR:

In the June number, 1911, of *THIS JOURNAL*, reference is made to phenol-formaldehyde condensation products invented by Mr. Aylsworth.

I am unable to find in the chemical literature any publication of Mr. Aylsworth relating to this subject, except a Belgian patent application dated February 11, 1911, No. 232,899, claiming International Convention Priority of one year, in accordance with a corresponding United States patent which has been applied for.

Belgium is one of the countries where patents are allowed without any preliminary examination whatever as to novelty, and where, furthermore, no restriction is put on the claims, nor the text of the patent,

the granting of the latter being a mere formality which places the claims of the applicant on record.

For persons who are not acquainted with the technical and chemical side of the subject, the long text of Mr. Aylsworth's Belgian patent is undoubtedly very complicated and liable to mislead. But when we come to the question of novelty, we find that the principal claim has for object the preparation of a hard, infusible condensation product by adding formaldehyde or its equivalent to a fusible phenol resin.

It so happens that this reaction was clearly disclosed in *THIS JOURNAL* about one year before the Aylsworth patent was filed: (See *Journal of Industrial and Engineering Chemistry*, Vol. 1, No. 8, August, 1909, L. H. Baekeland, "On Soluble, Fusible Resinous Condensation Products of Phenols and Formaldehyde," read May 14, 1909), from which I quote:

"In whatever way novolak be prepared, its properties are very distinct from those of bakelite and it cannot be transformed into the latter by simply heating. But I have found that by heating novolak in sealed tubes at 180°C ., under pressure with an excess of formaldehyde solution or any of the polymers of formaldehyde or other compounds which can generate formaldehyde, an infusible, insoluble mass is obtained that does no longer soften under the action of heat, as is the case for saliretin products, but which has all the characteristics of bakelite C."

The term novolak was the generic proposed name to designate all fusible soluble condensation products of phenols and formaldehyde of the type designated by Aylsworth as "phenol resin" or "resine phenique."

Furthermore, in patents granted to Baekeland in France (first addition to Patent 386,627, No. 11,628, filed January 22, 1909) and in Belgium (No. 213,576, published February 15, 1909) the invention is disclosed as follows:

"L'inventeur a trouve egalement que, au lieu de partir des phenols et de la formaldehyde, on peut commencer indirectement avec l'emploi d'un phenol-alcool ou ses equivalents, chauffant sept molecules de ce dernier avec au moins une molecule de CH_2O , ou une quantite equivalente de n'importe quelle substance contenant de la formaldehyde, ou capable de liberer cette derniere."

The "phenol resin" of the Aylsworth specification answers all the descriptions and all the properties published by Blumer. (See Eng. patent June 5, 1902, No. 12,880) and DeLaire (see French patent June 8, 1906, No. 361,539) and the description set forth in Baekeland's prior publication in *THIS JOURNAL*.¹

It is true that in the Aylsworth Belgian patent it is claimed that the fusible phenol resin has a molecular weight smaller than what I assigned to these products. On the other hand, it is stated that the molecular weight proposed by Mr. Aylsworth is based on "quantitative synthesis," whatever that may mean.

It should be pointed out that we have to deal here with substances which are amorphous, non-crystalline, non-volatile, and can not be purified by the usual ways. Furthermore, in any of these reactions, several substances are liable to be produced at the same time. These substances can form solid solutions one with another, or with any excess of the reacting materials employed.

Under the conditions, so-called "quantitative synthesis" would hardly be accepted in any scientific controversy, and specially not for determining the molecular weight.

The same can be said of any attempt to apply the other usual physical methods for the determination of molecular weights to similar substances unless the latter have been submitted to thoroughly careful purification. To omit this precaution would bring about such absurd results that it would only depend upon the operator to get almost any desired molecular weight by increasing for instance the amount of free phenol.

But the fact is undeniable that the physical and general chemical properties of the phenol resin described by Mr. Aylsworth correspond minutely to every prior description of these so-called fusible soluble resinous condensation products.

The Baekeland Belgian and French patents, as well as the corresponding Hungarian patent, mention the use of a phenol-alcohol, or its equivalents, heated in presence of formaldehyde or its equivalents. The phenol-resin described by Mr. Aylsworth is an equivalent of phenol-alcohol, as conclusively shown by DeLaire (see Eng. patent No. 15,517, 1905, and D. R. P. No. 189,262, 1905).

The dishydration of phenol-alcohol produces fusible phenol-resins, specially if a slight excess of phenol is present.

In the process described in Mr. Aylsworth's patent, hexamethylenetetramin is used instead of formaldehyde, but this hexamethylenetetramin is a well-known equivalent for formaldehyde, or better for a mixture of formaldehyde and ammonia. Whenever ammonia and formaldehyde are mixed together, hexamethylenetetramin is produced forthwith. So practically, whether you make a mixture of phenol and add formaldehyde, and then add ammonia, or whether you add ammonia to the formaldehyde first, or to the phenol first, and then afterwards add the formaldehyde, the mixture behaves entirely as if an equivalent amount of hexamethylenetetramin were used. This fact is in direct contradiction with the statement contained in Mr. Aylsworth's description, that no accelerating or condensing agent is used; indeed, the formaldehyde and the condensing agent, ammonia, are used here at the same time. In the Baekeland U. S. patent No. 942,809, ammonia is used as an accelerating or condensing agent, and it is expressly stated that the addition of the ammonia can be made at any stage of the reaction. As a further contradiction to the claim in the Aylsworth patent that no condensing agents are used there, it should be pointed out that a little further in the text, he mentions the use of amids of weak organic acids. But the value of these products as condensing agents has been disclosed in Baekeland's U. S. Pat. No. 942,809, in the text whereof it is stated that ammonia can be replaced by amines and amids of weak acids (see also Eng. Pat., Baekeland, No. 21,566, 1908).

Special stress is laid in the Aylsworth patent on the addition of substances which make, with the final product, a so-called solid solution, thereby increasing plasticity. This claim to novelty is also anticipated in some of my pending patents which have been filed at a date decidedly prior to Mr. Aylsworth's applications.

A special reference is made to the fact that in the Aylsworth process, the use of pressure can be dispensed with. In most of the processes described and patented by me, the use of pressure is only resorted to in special conditions in order to accelerate or expedite the process, but in many cases, is entirely dispensed with. Indeed, the use of small quantities of basic or alkaline condensing agents, which I was the

¹ *Loc. cit.*

first to publish and patent, enables to obtain rapid hardening at relatively moderate temperatures, which can be rapidly increased without the intervention of pressure. Nevertheless the process will be quicker and much more practical if at once the maximum temperature be applied and then, of course, pressure shows its strikingly favorable action. This pressure can then be applied in a hot hydraulic press or in a bakelizer, or any convenient way.

L. H. BAEKELAND.

YONKERS-ON-HUDSON, JUNE 12, 1911.

GEMS THAT RESEMBLE THE DIAMOND.

In spite of many seductive advertisements there is no gem that "*looks just like a diamond.*" Nor should we expect to find one, for, while two different substances may have a number of properties in common yet a study of *all* the properties of each will show many which differ. Still there are a number of gems which possess to a considerable degree some of the properties of the diamond and when well cut these gems can deceive and frequently have deceived those not expert in the determination of precious stones.

In times past such gems have even passed current as diamonds before the scrutiny of experts, for until the general spread of science, such tests as those of specific gravity, refraction, etc., were not applied, and many colorless zircons, topazes and sapphires probably passed as rather inferior diamonds. It is even claimed that the Braganza, a mammoth uncut gem among the Portuguese crown jewels, is merely a fine specimen of colorless Brazilian topaz, yet it has been listed for years among the world's greatest diamonds.

Among the gems which may be regarded as so closely resembling diamond as to be likely to deceive the inexpert, I will list and briefly discuss the following:

First, the colorless or pale zircon, sometimes called in the trade, the jargoon;

Second, the colorless sapphire;

Third, the colorless true topaz;

Fourth, the colorless beryl;

Fifth, colorless phenacite;

Sixth, colorless quartz.

These and a few other and rarer colorless gems constitute the list of gems that resemble the diamond. I may say at this point that none of them resemble the diamond to the casual glance so closely as does the very brilliant lead glass used in making the so-called "paste" or "strass" imitations so widely advertised and sold under various fictitious titles in many cities. This artificial material possesses a very high refractive index and is capable of separating the various colors of the spectrum so widely that it affords a brilliancy and "play" of colors that nothing but the diamond can equal. It is, however, deficient in hardness, being easily attacked by a file and consequently it does not long resist dulling and scratching from wear and hence does not hold its brilliancy. It is also easily attacked chemically by a number of things, with which it is likely to come in contact in wear and thus be still further dull. In many of the imitation diamonds the

tendency to scratch is partially prevented by using a thin slice of some hard gem material for the upper surface, making in other words a so-called "diamond doublet." This artificial gem has no real diamond about it of course, although formerly a few real diamond doublets were made in which the upper half of the stone was made of real diamond and the lower half of some less costly white gem, the two being joined at the girdle by means of gum mastic or other transparent cement. The modern diamond doublet usually has an upper surface made of a very thin slice of garnet, covering usually only the table, as the part subject to greatest wear. The garnet used is pale in color and so thin is the slice that hardly any color is visible. The remainder of the "stone" is entirely of lead glass. Some of these "works of art" are certainly very beautiful and at a reasonable distance they would probably puzzle an expert.

While none of the genuine gems I have listed quite approaches the "paste diamond" in play of colors, many of them are nearly as brilliant in the lively play of white light which they afford when cut in a manner suited to such material, which cutting, by the way, should not be just like that most suited to the diamond.

In regard to the order of precedence among them, I should put the colorless zircon first. This gem possesses adamantine luster in a high degree, that is, the amount of light reflected from its *top* surfaces, when properly inclined to the light, approaches closely to the amount reflected by a genuine diamond surface. This effect must not be confused with the brilliancy of the flashes of light reflected from the *interior rear* surfaces of the stone. That is another matter. This adamantine luster gives what the French call *éclat* to the zircon. It is snappy, cold and glittering in its luster. So closely does it resemble diamond in this respect that I was able to deceive a diamond cutter in one of the best establishments in this country by a brown zircon which I wore in my scarf this summer. He referred to it as my "brown diamond" although he was not above four feet away and looking squarely at it. Of course in a stone of positive color, no large amount of prismatic "play" is possible or expected, and so the lack of it in my brown zircon was not felt. The cutter would doubtless have detected the difference in a colorless zircon but one not so expert might not.

Of course, in hardness, in specific gravity and in refraction, the zircon is not like the diamond. It is much softer being only 7.5 as against 10 in hardness by Moh's scale; its specific gravity is 4.4-4.7 as against 3.5-3.6 for diamond; and it is doubly refracting while diamond is singly refracting. It could thus be readily distinguished by any one who understood the application of the tests for the above properties.

After the zircon in order of excellency I would place the white sapphire. Its index of refraction is higher than that of any of the other gems in my list except the zircon, and its great hardness renders it capable of taking and holding a polish almost equal to that of the diamond. It does not possess the adamantine luster, however. Its luster is probably best defined

as splendid. It exceeds the luster of glass and of the other gems in my list which have what is usually styled the vitreous luster. Both the zircon and sapphire when well cut and pure white show a faint "play" of colors and both give fine brilliancy in their reflections of white light. I have fooled many retail jewelers with a fine specimen of white sapphire which I have set in a ring. As in the case of zircon, so with the sapphire, a test of its hardness, specific gravity and refraction will at once serve to distinguish it clearly from diamond. Its hardness is 9, its specific gravity 3.9-4.1 and it is doubly refracting.

Next to the zircon and sapphire I would place the white topaz. It gives a faint play of color, is hard enough to resist wear for years and takes an extremely high polish. Many so-called "white topazes" advertised by unscrupulous dealers are only lead glass, and many more are cut from the softer and cheaper rock crystal. I had one of the latter sent me recently under a guarantee that it was a genuine white topaz. It was a finely cut and very brilliant gem but it was *not real topaz*. I sent it back after a specific gravity test, which I recorded on the inside of the paper in which the gem was wrapped, saying that I was sorry but I couldn't use "that kind."

I have already referred to the Portuguese "Braganza" as probably a white topaz. The fact that the specific gravity of topaz is very nearly that of diamond makes it a still more dangerous imitator, but its hardness of 8 and its double refraction serve to distinguish it.

The other colorless gems in my list, phenacite, beryl and rock crystal very closely resemble each other and all give brilliant stones when properly cut. The phenacite and beryl are but slightly softer than topaz and would wear well. The rock crystal is the softest in my list, and while it will hold its brilliancy for some time it would dull in the course of a few years or even months if subjected to hard wear as a ring stone.

Aside from the peculiar interest which attaches to these colorless stones from the fact that they may be and doubtless many times in the past have been substituted for diamond either ignorantly or with purpose to deceive, there is, I believe, a worthy interest in them for what they really are and for the real beauty which they undoubtedly possess.

When men shall have learned to practice honesty as the best policy, it is to be hoped that these gems, which do truly somewhat resemble the diamond, but which resemble each other more, may come into their own and be appreciated and valued for their own beautiful qualities.

COMMERCIAL TURPENTINES OF UNITED STATES.¹

The turpentine-producing area in this country is practically confined to the coastal plains region of the Southern States. In the earlier days the industry was best developed in North Carolina, but owing to destructive methods of turpentine orcharding, in conjunction with lumbering, fires, etc., the industry has gradually worked southward and westward, until at

present Florida produces the most turpentine, followed by Georgia, Alabama, Mississippi, Louisiana, North Carolina, South Carolina, and Texas, in the order named. The statistics of production in various years from 1870, taken from the census reports, are given in the following table:

Year.	Gallons.	Value.
1870	6,004,887	\$ 2,194,498
1880	17,565,250	1,542,120
1890	17,316,200	5,459,115
1900	38,488,170	\$14,960,235
1905	30,687,051	15,170,499
1908	36,589,000	14,112,400

It is the trade practice to grade turpentine according to its color, and the various grades are known as "water white," "standard," "off one shade," "off two shades," and "off three shades." The latter is not merchantable. Under the trade regulations the deductions in price on turpentine off one shade is 2.5 cents per gallon and off two shades 4 cents per gallon.

About half of the turpentine produced in this country each year is exported, chiefly to Europe, while by far the larger part of the remainder is consumed in the varnish and paint industries, and small quantities are used in medicine and as a solvent for gums, rubber, fat, and waxes in this country. No statistics are obtainable showing the quantities consumed for the latter purposes, nor in thinning paints and varnishes at the time they are actually used. The distribution of turpentine produced in 1905 was as follows:

	Gallons.
Produced	30,687,051
Exported	15,894,813
Used in manufacture of paints and varnishes ..	7,160,774
Used in other industries (by difference)	7,631,464

The turpentine found on the American market is quite frequently adulterated with cheaper and inferior oils, those most commonly employed being the petroleum oils having specific gravities corresponding closely to that of turpentine, and distilling at about the same temperature. Other adulterants are certain coal-tar oils, rosin spirits, and wood turpentine, which closely resemble turpentine in specific gravity, distilling temperature, and some other properties.

It is quite common for druggists, both wholesale and retail, to buy turpentine from oil and paint dealers or from any one handling it in large quantities, and, therefore, samples have been secured from oil and paint dealers, as well as from druggists, their stock being in many instances representative of the turpentine sold at the drug stores in the same community. In fact rarely is any distinction made between turpentines for drug or technical purposes.

Though it is known that spirits of turpentine is very frequently adulterated, no systematic investigation of the subject in this country is on record. For this reason, the results obtained on samples collected from all parts of the country are recorded for the information of the public, to show the extent of the practice of adulteration, and to furnish more complete data for the grading of American turpentine and the preparation of specifications therefor which shall be

¹ Abstract from monograph prepared in Bureau of Chemistry, Department of Agriculture, by F. P. Veitch assisted by M. G. Donk.

fair to the producer and also insure that the consumer secures the article for which he pays.

Straight wood turpentine are readily distinguished from gum turpentine by their odor, or when they have been very carefully refined, by the odor of the first fraction, or of the residue from fractional distillation. One or both of these portions have the peculiar "sawmill smell," and the residue has a camphoric and somewhat nauseating odor characteristic of wood turpentine, which is quite different from the mild, sweet fragrance of gum turpentine.

Destructively distilled wood turpentine and also rosin spirits are more readily distinguished from gum spirits by their odor than is wood turpentine prepared by steam distillation, and they also give distinguishing color reactions when mixed with sulphurous acid as suggested by Hertzfeld or with hydrochloric acid.

Turpentine adulterated with more than 10-20 per cent. of coal-tar oils, or of gasoline or kerosene which have not been deodorized, may usually be readily detected by the characteristic odor of the mixture. The odor of rosin spirits, while quite distinctive, is difficult to detect in mixtures with turpentine. The presence of petroleum oils is also indicated by bubbles or "beads" persisting for a few moments on the surface of the turpentine shaken in a partly filled bottle.

The presence of more than about 10 per cent. of kerosene or similar mineral oils is readily detected by the spot which a few drops of the sample placed on white paper leaves on drying. Gasoline and other light mineral oils do not leave this spot.

The detection of mineral oils in turpentine is relatively quite simple, and is accomplished by mixing the turpentine with a certain proportion of sulphuric acid of a given strength, in which the turpentine is destroyed and mixes with the acid while most of the mineral oil remains unaffected and separates in a layer on top of the acid.

Only a few of the samples taken of producers' goods are adulterated with mineral oils, while the turpentine of the primary buyers and dealers in the turpentine belt is adulterated extensively, showing 13.6 and 18 per cent. of adulterated samples, respectively. The dealers' samples contain a much higher percentage of the adulterant than either of the other two classes, exceeding the producers' goods by 3.5 and the primary buyers' goods by 4.2 per cent. Adulterations occur more frequently and are present in larger quantities outside the turpentine-producing belt than within it. Eighteen per cent. of all the samples collected were adulterated, and the average percentage of adulterant in these was 6.1 per cent., ranging from 1-71 per cent. in the individual samples. The average amount of mineral oil in a barrel of the adulterated samples was approximately 3 gallons, which, basing the calculation simply on the cost of the two materials, made these adulterated turpentines worth fully \$1.50 less per barrel than unadulterated stock. These facts assume graver significance when it is remembered that turpentine is an article so well known and so generally used that it is carried in stock and sold by merchants

generally, particularly by country merchants, and when bought from any source is liable to be employed indiscriminately, either medicinally or technically.

The consumption of turpentine in the United States during 1908 was approximately 15,000,000 gallons. If 18 per cent. of this was adulterated, then approximately 3,000,000 gallons of adulterated turpentine, containing an average of at least 6 gallons per hundred of mineral oil, costing about one-fifth as much as the turpentine, was sold at turpentine prices.

CYANAMID IN AMERICA.

There are now twelve factories engaged in the manufacture of cyanamid (lime nitrogen), and one or two others in the course of construction with an aggregate present and projected capacity of about 250,000 tons. These factories are scattered throughout Europe with the exception of the American Cyanamid Company which is located at Niagara Falls, Ontario. The American Company which has been operating since January, 1910, now has a capacity of approximately 13,000 tons a year. The product is somewhat more highly developed than much that is produced abroad, due to the requirements of the American market—that it shall be capable of being compounded into complete fertilizers. The free lime which constitutes a considerable percentage of "Cyanamid" is hydrated, and it also undergoes a further treatment to eliminate to a large extent the dust nuisance which was so objectionable in the original product.

The plant at Niagara Falls is of a most substantial character, the buildings being entirely of concrete and steel even to the roofs. Power is the chief single item of expense, and as the factory runs every minute of the day, 365 days in the year, it must be had continuously and cheaply. The process as followed by the American Cyanamid Company consists of the making of calcium carbide, which is pulverized and treated in electric ovens to nitrogen gas under pressure. The nitrogen gas is derived from the atmosphere, being a modification of the well-known copper process. The American Cyanamid Company is, with one or two exceptions, the only cyanamid factory which does not use the liquid air process for the manufacture of its nitrogen.

The price per unit of ammonia at Baltimore, the chief distributing point, was fixed early in the past season at 20 to 25 per cent. in excess of the ruling price for sulphate of ammonia and has been maintained at that figure. If cyanamid can eventually be sold at prices materially cheaper than other nitrogenous fertilizers, its utilization on a very large scale would appear extremely probable.

As yet, we have very little data from field tests in this country to determine the efficiency of cyanamid as a crop-producer as compared with other nitrogenous fertilizers, but the agricultural departments of Europe have done considerable work along this line during the past four or five years, and the results have for the most part been very favorable.

The comparative efficiency of nitrogenous fertilizers is affected by the nature of the soil and the

character of the season, and in the tests made the results obtained vary considerably. It is only by careful experiment that it can be definitely known which fertilizer is likely to be most profitable for a certain soil. Cyanamid has not been used as a fertilizer but for only a comparatively short time, and further

The imports of silk goods for the same period show a variation from year to year but no increase in the last 30 years. The average for that term has been about \$32,000,000 a year, the average for the period 1880-'89 being \$33,000,000. Thus on a basis of factory and import prices the per capita expenditure in 1880 was



experiment and utilization are necessary to establish its relative merits as compared with other nitrogenous fertilizers. The reports of experts, however, who have experimented in European countries with cyanamid agree to its value, and it would appear that in certain soils it produces as good, if not better, results than other nitrogen-yielding fertilizers.

Cyanamid contains about 60 per cent. of lime, and like nitrate of calcium is especially adapted to soils deficient in that element. Its action is less rapid than that of nitrate of soda, but is continuous and lasts longer. One hundred and sixty American fertilizer companies are now using the product made at Niagara Falls as a source of nitrogen in their complete fertilizers.

SILK INDUSTRY INCREASED \$90,000,000 IN TEN YEARS.

In a bulletin issued by the Bureau of the Census the statement is made that "the development of the silk industry of the United States during the last few years is one of the most interesting features of the country's progress." Reference to the records of the trade shows the product value of the industry for the years indicated as:

1869.....	\$ 12,210,000
1879.....	41,033,000
1889.....	87,298,000
1899.....	107,256,000
1904.....	133,288,000
1909.....	196,425,000

\$1.45 and in 1909 it was \$2.50. The greatest gain in the last 10 years has been made in the output of dress goods, which in 1909 represented 55 per cent. of the entire product value. Ribbons represented 17 per cent. of the total value, velvet and plushes 7 per cent., and laces, braid and trimmings 5 per cent. The output value of dress goods doubled in 10 years.

It appears that the product value of the 186,000,000 yards of dress goods made in 1909 averaged 58 cents a yard, while the value of the 88,000,000 yards made in 1899 was 60 cents. The supply of animal silk has more than doubled in the last 20 years, and the price of the commodity shows little or no increase in that time; yet so sharply has demand followed supply that, as stated by the Bureau of the Census in an earlier report, "ingenious efforts have been made to discover a substitute for the animal product, and the manufacture of artificial silk is assuming considerable importance." At present the chemically made substitutes are used chiefly in the manufacture of braids and trimmings.

Of the 843 silk mills of the country, 347 are located in New Jersey, 219 in Pennsylvania, 168 in New York, 47 in Connecticut, 19 in Massachusetts, and 13 in Rhode Island, leaving only 30 located elsewhere. The New Jersey product is valued at \$65,000,000, that of Pennsylvania at \$62,000,000, of New York at \$26,500,000, of Connecticut at \$21,000,000, thus making for those states 95 per cent. of the entire product.

Massachusetts produces a little less than 5 per cent. The notable increase in the industry in the last 10 years has been in New Jersey and Pennsylvania where, on a basis of product value, the honors are about equally divided. Imports of raw silk, admitted free of duty, are valued at about \$75,000,000 a year, nearly 60 per cent. of the total being bought in Japan. The remainder comes chiefly from Italy and China.

The bulletin notes that "with the possible exception of China, for which no complete statistics are available, the United States is now the largest silk manufacturing country in the world. This position has been taken from and maintained against France, since 1905."

IMPORTANT DECISION OF THE SUPREME COURT OF THE UNITED STATES UNDER THE NATIONAL PURE FOOD AND DRUGS ACT.

Together with its trust decision the Supreme Court handed down, on May 29th, a most important decision in the case of Dr. O. A. Johnson, of Kansas City, Mo.

Johnson was indicted in the Federal courts of Missouri in 1909 on a charge of having violated the Pure Food and Drugs Act of 1906. It was alleged that Johnson, doing business under the name of a company, shipped from one State to another certain articles designated as "cancerine tablets," etc., the labels upon which were false and misleading in that they implied that the articles would cure and were effective in bringing about the cure of cancer. It was alleged in the indictment that this statement was untrue and the articles were worthless and ineffective for such purposes.

The Supreme Court decided that provided there is no misstatement on the bottle or package as to its contents, the manufacturer is free to sell his goods. Justice Holmes announced the majority opinion, Justice Hughes delivering a dissenting opinion in which Justices Harlan and Day concurred.

The court acknowledged that "in a certain sense the statement on the label was false, or, at least, misleading," but it held that the language of the pure food law is such that the statement contained therein as to the meaning of misbranding "is aimed not at all possible false statements, but only at such as determine the identity of the article, possibly including its strength, quality and purity."

If a label were to state that the contents of a bottle was water when as a matter of fact it was other than water, it would come under the misbranding in the meaning of the law, according to to-day's opinion. But the opinion adds that when the statement on the box or bottle of medicine is "shown to be false only in its commendatory and prophetic aspect," it did not come within the act.

This decision appears to be of importance for the patent medicine business in the United States and is a defeat for the government officials in charge of the National Pure Food and Drugs Act who always claimed that labels must not bear any inferences as to "cures," etc., because such claims were misleading and false.

A NEW CANE SUGAR PROCESS.

A new process of sugar-making is being tried by one of the large sugar companies in Cuba. In the ordinary process the juice is extracted from the cane by pressing it between sets of rollers. In the new process the cane is broken up, dried and finally treated by a diffusion or a solution process, similar to that used in treating sugar beets, which recovers a larger proportion of the juices than can be recovered by squeezing between rolls.

The cane is fed to a disintegrating machine having drums, 4 feet diameter, which are fitted with teeth and have a peripheral speed of about 6,500 feet per minute. The cane is thus broken up very small, about half the product resembling coarse sawdust while the remainder consists of short thin fibers. The two kinds of material may be separated in a revolving screen or may be handled together. This product is fed by force-feed rollers into drying kilns where it travels back and forth on conveyor belts running in opposite directions. These belts are staggered about 18 inches and the material from each belt falls to a lower one running in the reverse direction. Air heated to about 190° by exhaust-steam radiators is admitted to the kilns and is further heated to 240 or 250° by means of live-steam coils. The feed of material into the kiln and the speed of the belts in the kiln are under the control of the operator, who also controls the admission of exhaust steam to the radiators and live steam to the superheating coils.

The dried material is discharged from the lowest belt onto a transverse elevating conveyor which delivers it to a compress or baler; the bales are about 14 × 18 × 36 inches, with a density of about 50 lbs. per cubic feet. The material can then be stored or sent direct to the refinery, where the sugar is extracted by the diffusion process. The pulp remaining contains but a very small proportion of sugar (only a fraction of 1 per cent.) and it is suitable for paper-making with much less cooking than is required with ordinary material. The process is the invention of Mr. Geo. W. McMullen, of Chicago, and the first plant is now in experimental use at a mill of the Nipe Bay Co. The machinery was built by Roberts Brothers, of Chicago.

Under the ordinary roller process the cane is fed in layers, 6 or 8 inches thick, to a set of three large rolls (two lower and one above); these crush and compress the cane and expel the juice. The crushed cane then goes to a second set of rolls and more juice is expelled, but after all the rolling the crushed waste material or "bagasse" contains a considerable proportion of sugar (from 15-30 per cent.). Much of the bagasse is fed to the furnaces, but is so wet that a considerable amount of wood is required to make it effective as fuel.—*Engineering News*.

RADIOACTIVE INVESTIGATIONS IN RUSSIA.

Special Correspondent.

Although Russia is rich in mineralogy embracing a number of the known rarer metals, it is generally deplored among Russian scientists that in that country

practically nothing has been done to meet the demand that has arisen for minerals of a radioactive nature. Therefore the Imperial Russian Technical Society may be congratulated on such steps as it has taken towards the study of radioactivity. It is even stated in a report on the Odessa laboratory, which has been specially established for the purpose of investigating supposed radioactive minerals, that no deposit of ore has been discovered in the country of a radioactive nature and even the mineral water wells have not been investigated.

On the initiative, however, of E. S. Burkser, the Odessa section of the Society proposed to establish a laboratory for the specific object of investigating the radioactive minerals of Russian springs and earths and particularly those of the estuary on which Odessa is situated. In a land so rich in open mines as Russia it is impossible to assume the absence of radioactive minerals and therefore the radioactive laboratory appealed to mining engineers, to the Geological Committee and others to send on to it for investigation, which it would conduct free of charge, minerals and ores in which the presence of uranium or thorium might even be only suspected. For guidance in the investigations a table of uranium and thorium ores has been issued translated from the French. In order to insure an efficient equipment of a laboratory the Technical Society sent the manager of the laboratory, Mr. E. S. Burkser, to France and Germany to learn the technique of radiological investigation. At the present moment the necessary apparatus is being installed for the investigation of radioactive earths, water, and powerful radioactive substances, and investigators are already examining the mud and the water of the Odessa estuary. In November, 1910, Mr. E. S. Burkser made a statement of the chemical section, of the results of his investigations into the radioactivity of the town supply water.

On the suggestion of institutions and private persons the laboratory will investigate the radioactivity of various substances at a fixed tariff (presumably this has reference simply to those persons seeking information for commercial purposes). The tariff of radiological investigation for water in Maxe units is 15 roubles for muds; and for earths 7 r.; for determining emanations proceeding from mud or earth, from 20-50 r.; and for determining the radioactivity of minerals or radioactive medicines (not lower than 0.1 uranium units for medicines) in uranium units, 7 r. It may be added that the Imperial Russian Technical Society also has a technico-chemical laboratory in St. Petersburg for scientific and industrial purposes. But the Odessa institution appears to be the only one founded and equipped for the specific purpose of investigating the radioactive resources of Russia.

RUBIDIUM AND CAESIUM FELDSPARS.

Special Correspondent.

An interesting note was presented to the St. Petersburg Academy on 23rd March/5th April on rubidium and caesium feldspars by V. I. Vernadsky. He states that "the unexpected cessation of my pro-

fessional work in the Moscow University forced me to abandon several experiments at quite a incompleting stage. Among these experiments I should like to observe my initial work on the synthesis of rubidium and caesium orthoclases because I note that in this direction other work is being done. The effort to synthesize $\text{Rb}_2\text{Al}_2\text{Si}_2\text{O}_{10}$ and $\text{Cs}_2\text{Al}_2\text{Si}_2\text{O}_{10}$ were begun by me in view of the following considerations: caesium and rubidium are widely distributed in feldspars. (Regarding this distribution see V. Vernadsky's works in the Geological Museum of the St. Petersburg Academy, 1908, page 88; also his notice to the Academy of Science, St. Petersburg, 1909, pages 163 and 822.¹ In this article the book references are given.) It must be supposed that they are found in the formation of isomorphic mixtures corresponding in composition to potassic feldspar (orthoclases and microclines), that is, we have here a body of the type $(\text{K}, \text{Rb}, \text{Cs})_2\text{Al}_2\text{Si}_2\text{O}_{10}$. As is known orthoclases generally after fusion do not yield crystals, but the fusion possesses a glassy composition. One may therefore suppose that the crystallization of this body is assisted by the presence of caesium and rubidium, while it would be interesting to investigate the caesium and rubidium orthoclases also for the explanation of the causes of the variations in the properties of orthoclases, which do not result from the presence in the isomorphic mixtures of sodium and calcium-alumosilicates to be found in them.

"My preliminary experiments made with the addition of rubidium (either in the form of Rb_2CO_3) to the orthoclase testify to the favorable influences of these bodies on the crystallization of orthoclase. The fusion of rubidium corresponding to the theoretical composition (of $\text{Al}_2\text{O}_3\text{SiO}_2\text{Rb}_2\text{CO}_3$) also appears crystalline. Unfortunately I was not able to make more particular investigations on this point. The experiments of caesium were only begun, and definite results were not obtained, but apparently caesium acts similarly to rubidium."

HYDROXIDE OF CHROME TO BE ADMITTED DUTY-FREE.

The United States Court of Customs Appeals, the highest instance in tariff matters, rendered a decision on June 2nd, in which the Board of General Appraisers' opinion on the classification of hydroxide of chrome was affirmed; as a result this material will be placed on the free list under Section 499 of the Act of 1909, as an article in a crude state used in dyeing and tanning.

The importers claimed that this substance which is won as a by-product in the manufacture of anthraquinone from anthracene by means of oxidation with bichromate of soda in sulphuric acid solution was not a chemical compound to be assessed for duty at 25 per cent. *ad valorem*, but an article in a crude state used in dyeing and tanning.

The court held that the article as imported is certainly in a crude state in two respects: First, the article itself is in the state of its first production,

¹ W. Vernadsky and E. Revousky in the *Comptes Rendus de l'Acad. d. Soc. de Paris*, December 27, 1910.

without being refined by additional treatment applied for that purpose. In this condition it is mixed with various impurities. This is worthy of notice, although it may not be the controlling consideration with the purview of paragraph 499. The filtering and washing process described in the testimony had no effect on the article itself, other than "to get it by itself."

Second, it is an article in a crude state within the meaning of the paragraph because as imported it is not in a condition fit for use in dyeing or tanning, but it is only a raw material which is to be converted by further treatment into other articles fit for such use. This is the important aspect in which the article may be said to be in a crude state. The paragraph treats of materials which are used in dyeing and tanning.

The importation is simply a raw material in its relation to those uses and is therefore in a crude state in that respect. To prepare it for such uses other chemical elements must first be added to it, so that when finally used for such purposes it presents a different chemical combination.

The court finds that this substance is used in this country as a mordant in the printing of textile fabrics and in tanning. In neither case, however, it is claimed, is it used in the form in which it is imported. For use in tanning it is treated with sulphuric acid, forming a sulphate of chrome. In all its uses it appears that the article imported has to be converted chemically into new and different combinations.

THE ORIGIN OF HYDROCARBONS.

In Bulletin 401 of the United States Geological Survey, entitled "Relations between Local Magnetic Disturbances and the Genesis of Petroleum," by George F. Becker, the condition of knowledge with reference to the origin of petroleum and other bituminous substances is reviewed. Some oils, says Mr. Becker, are undoubtedly organic and some are beyond question inorganic. They may have been derived from carbonaceous matter of vegetable or animal origin, and they may have been derived from carbides of iron or other metals. It is also barely possible that the hydrocarbons exist as such in the mass of the earth.

While studying the subject, Mr. Becker was led to inquire whether any relation could be detected between the behavior of the compass needle and the distribution of hydrocarbons. Not much could be expected from a comparison of these phenomena, for magnetite exerts an attraction on the needle whether this ore occurs in solid masses or is disseminated in massive rocks; moreover, many volcanic rocks possess polarity. In glancing over a map of the magnetic declination in the United States Mr. Becker found that the irregularities of the curves of equal declination of the compass were strongly marked in the principal oil regions. The most marked agreement is found through the great Appalachian oil field, which is the area of greatest variation in declination. In California, also, strong deflections accompany the chain of hydrocarbon deposits.

These observations are to some extent also supported by conditions in the Caucasus, where great magnetic disturbances exist. While the theory of the inorganic origin of the hydrocarbons as exploited by various scientists is not proved by this study, yet the contention that great oil deposits are generated from iron carbides is strongly borne out by a study of the map of magnetic disturbances in the United States. The map shows that petroleum is intimately associated with magnetic disturbances similar to those arising from the neighborhood of substances possessing sensible magnetic properties, such as iron, nickel, cobalt, and magnetite.

VANADIUMISM.

Dr. Walton Forest Dutton, of Carnegie, Pa., describes in *The Journal of the American Medical Association*, June 3, 1911, under the above name, a new industrial disease of interest to chemists, caused by the exposure to dust and fumes of the various vanadium compounds, especially vanadium trioxid.

Vanadiumism is a chronic intoxication, of which the symptoms are emaciation, an anemia not altogether unlike chlorosis, a dry irritating paroxysmal cough, sometimes so intense that hemorrhages result, irritation of the nose, throat and eyes, gastro-intestinal involvement demonstrated by nausea and diarrhea, followed by obstinate constipation. Albumin, casts and blood are often present in the urine.

In the absence of grave, renal, blood, nervous and lung involvement, the prognosis is good, but where there is active inflammation of the kidneys and lungs it is unfavorable. Dr. Dutton states that the prevention of vanadiumism is difficult in vanadium works, owing to the carelessness of employees and employers. Means to allay and carry off the dust and fumes should be employed constantly. Perfect ventilation and the use of respirators are imperative. The nasal and oral cavities should be thoroughly cleansed with some efficient alkaline spray, such as the ordinary Dobell solution, followed by a mentholated oil spray. The stomach should be washed out, and later the intestines freely evacuated with a saline laxative. The cough may be allayed by giving terpin hydrate $\frac{1}{4}$ grain, heroin $\frac{1}{8}$ grain, and creosote $\frac{1}{2}$ minim, every two hours with counter-irritations of iodine or mustard applications over the chest. The inhalation of stimulating vapors is salutary. Iron, calisaya, and strychnin will meet the needs of anemic, nervous and debilitated conditions. Codliver oil may be given with advantage. Active outdoor exercises are essential. Turkish, Russian or cabinet baths may be given to aid elimination.

ADRENALIN AND A NEW MEMBER OF THE "DIGITALIS SERIES."

One of the most interesting investigations of modern times has just been carried out and published in the May 27, 1911, number of *The Journal of the American Medical Association* by John J. Abel and David I. Macht, of Johns Hopkins.

In examining the convulsant action of certain organic dyestuffs, the authors had the opportunity of trying the effect of these substances on a tropical toad, *Bufo Agua*. Scraping off some of the milky secretion which exudes from the parotid gland of the animal with an iron knife, the authors noted a bluish green discoloration on the blade. This observation led them to test the diluted secretion with ferric chloride, whereupon the characteristic green color of the pyrocatechin reaction was developed. As this reaction is given by the active principle of the suprarenal glands it was soon demonstrated that the secretion contained a substance identical with epinephrin (adrenalin).

Quantitative experiments showed that the secretion contained rather large amounts of this substance (0.3 per cent. in the suprarenal glands of beeves and about 5 per cent. in the secretion) and since the secretion is obtained by squeezing (or milking) the parotid gland, it is not at all impossible that this toad may be utilized in the future for furnishing the raw material for the production of adrenalin.

Associated with adrenalin in the venom of the toad is a digitalis-like substance, to the presence of which the secretion of the toad owes its efficacy as an arrow poison. The authors call this new material "Bufagin" and give it the formula $C_9H_{12}O_2$.

If the content of adrenalin is 5 per cent. in the secretion, bufagin occurs in it to the amount of 36 per cent. Pharmacological experiments showed that bufagin is one of the most effective members of the digitalis series.

The toads which were experimented upon were obtained from the neighborhood of Montego Bay, Jamaica, where they are popularly known as bullfrogs.

A PRACTICAL MANUFACTURER ON THE SYNTHESIS OF RUBBER.

In the May number of the new journal *Kunststoffe*, Dr. Gerlach-Hannover, a practical rubber manufacturer, makes the following statement:

"The problem of producing caoutchouc synthetically has been solved. But just as in the case of indigo, 20 years lapsed before the synthetic product was successfully launched, it will take at least 20 years before synthetic rubber will make its appearance commercially. It will take perhaps longer with caoutchouc because the physical properties of this material are not as well known as those of indigo. The high price of the natural product, stimulated research and after the pioneering experiments of Harries, the Elberfeld Farbenfabriken have finally succeeded in producing larger quantities of a product derived from a material closely related to isopren. At this stage of the development it was found out that there exist many sorts of rubber which are near relatives, but still possess different characteristics.

"The first synthetic caoutchouc which was placed at my disposal, for example, did not unite with sulphur and had a leathery appearance. This was not to be wondered at, as there are known some varieties of natural caoutchouc which cannot be vulcanized.

Soon another sort of rubber came to my notice which showed better affinity for sulphur, but still could not be perfectly vulcanized. Above all it lacked elasticity. Soon, however, larger quantities of a third sort were submitted to me which to my great astonishment showed all the excellent properties of natural rubber.

"But now the question arises whether this material of the Elberfelder can be economically produced on a large scale and may thus become a danger for natural rubber. It cannot be denied that the substance, which possesses good qualities, can be utilized for practical purposes. Its price is not high but it is a complex question to decide whether this synthetical product will become a danger to natural rubber. All kinds of economical and commercial conditions must be taken into consideration. One thing, however, is certain, that synthetic rubber will soon be a commercial article."

WEARING AWAY OF MOTHER EARTH.

Investigations by the United States Geological Survey of the erosion of numerous drainage basins of the United States show that the surface of the country is being removed at the average rate of about an inch in 760 years. Though this amount seems trivial when spread over the surface of the country, it becomes stupendous when considered as a total, or even in separate drainage basins. Mississippi River, for instance, carries annually to the sea 136,400,000 tons of dissolved matter and 340,500,000 tons of suspended matter, and of this total Ohio River carries 83,350,000 tons and Missouri River contributes more than twice as much. Colorado River, which has built up for itself a vast delta, brings down more suspended matter than any other river in the United States; delivering annually 387 tons for each square mile of its drainage basin, or a total of 100,740,000 tons.

The rivers of the United States carry to tidewater every year 270,000,000 tons of dissolved matter and 513,000,000 tons of suspended matter. This total of 783,000,000 tons represents more than 350,000,000 cubic yards of rock, or 610,000,000 cubic yards of surface soil. If this erosive action had been concentrated on the Isthmus of Panama at the time of American occupation it would have excavated the prism for an 85-foot level canal in about 73 days.

GLASS MACHINE COMPANY INSOLVENT.

On May 18th involuntary bankruptcy proceedings were filed in the United States District Court at Pittsburg against the Colburn Machine Glass Co., on petition of The Star Glass Co., of Reynoldsville, Pa., The H. L. Dixon Co. and The Pittsburg Clay Pot. Co., of Pittsburg, and The Dover Fire Brick Co., of Cleveland, Ohio, whose aggregate claims amount to \$12,037.07.

These proceedings have to do with the sheet glass drawing process upon which the eyes of glass manufacturers throughout the world have been centered for upwards of a decade, which at various times has been

prematurely reported as having reached a stage of commercial success. While it is true that some window glass was manufactured by the process, the invention is still in an incomplete state and opinion is divided as regards the practicability of the idea. Some very competent authorities are still of the opinion that success could be wrested from failure if capital for continuing experiments could be obtained, while others look upon the proposition as a closed incident. The experimental plants at Franklin and at Reynoldsville were mechanical marvels which challenged the admiration of all who were privileged to witness their operation, but, as is indicated in this bankruptcy proceedings there was always something radically wrong which hundreds of thousands of dollars were unable to correct.

ACETPHENETIDIN LABELING DECISION.

In the case which the government had brought against the Antikamnia Co., the Supreme Court of the District of Columbia rendered a decision on May 29th, in favor of the Antikamnia Co. The question at issue was whether, under the National Pure Food and Drugs Act, the Antikamnia Co. was obliged to add on their label to the word of "Acetphenetidin" the legend "derivative of acetanilid."

The Antikamnia Co. prevailed against the government in their claim that the law does not require any such addition and that it was not the intent of Congress to demand that the name of the drug from whence it is derived should also be recited to properly label a headache powder.

It should be borne in mind that this decision was rendered in a demurrer case in which the fact that acetphenetidin was a derivative of acetanilid was technically conceded for the purpose of the arguments.

In reality, the Antikamnia Co., if unsuccessful in the demurrer, would have carried on the litigation on the theory that acetphenetidin is not a derivative of acetanilid and is not manufactured commercially from acetanilid and cannot be so produced unless acetanilid is first destroyed. In consequence of this decision, headache powders containing acetphenetidine need only bear on the label a statement of the quantity of acetphenetidine present.

"SOLIDIFIED" GASOLINE.

The *Automobile* states that this substance, the invention of a Roumanian chemist, Dr. V. Rosculetz, is the result of dissolving stearic acid (which has undergone prolonged treatment with hydrochloric acid at a high temperature) in the hydrocarbons to be solidified, the solution being mixed with an alcoholic solution of caustic soda at about 175° F. This mixture cools to a stiff, jelly-like mass, capable of being carried about and handled like any other solid body. Solidified gasoline is not a chemical combination, as the gasoline can be completely evaporated from it. Under the microscope it appears to have the structure of an extremely fine sponge, the pores of

which hold the gasoline in an unchanged form, the mass representing about 99 per cent. gasoline and 1 per cent. stearic acid and soda. The physical properties are the same as those of liquid gasoline, evaporation is easy, and the inflammability and carbureting power are very intense. Upon heating, it does not melt at ordinary pressures, but evaporates slowly; when ignited it burns like wood or coal, and the flame can be extinguished by water or by smothering with a cloth. It is stated that the volume of the solidified gasoline is from 10-20 per cent. less than that of the gasoline used in its preparation.

SILVER, COPPER, LEAD AND ZINC PRODUCED IN CENTRAL STATES IN 1909.

The final figures of the production of silver, copper, lead, and zinc in the Central States during 1909, compiled by C. E. Siebenthal and B. S. Butler, of the United States Geological Survey, have just been published and may be had on application to the Director of the Survey at Washington. The production by mines of these metals in Arkansas, Illinois, Iowa, Kansas, Missouri, Oklahoma, and Wisconsin is discussed by Mr. Siebenthal and that in Michigan by Mr. Butler.

The total production of the four metals in the States named in 1909 was \$63,992,548, as compared with \$56,326,703 in 1908. The production for 1907 was \$77,697,457.

The following table shows the values by States for 1908-9:

	1908.	1909.
Arkansas.....	\$ 58,130	\$ 57,144
Illinois.....	196,001	259,000
Iowa.....	41,414	6,876
Kansas.....	1,538,698	1,347,860
Kentucky.....	7,772
Michigan.....	29,601,603	30,586,693
Missouri.....	22,256,571	27,776,284
Oklahoma.....	575,330	1,137,770
Wisconsin.....	2,058,956	2,818,100
	\$56,326,703	\$63,997,999

EXPORT STATISTICS.

According to a statement of the Bureau of Statistics the fiscal year ending with the present month will show some remarkable records on the subject of exports and imports. The statement sets forth that for the first time in the history of the United States the export trade of this country this year will go beyond the \$2,000,000,000 mark.

The figures covering a period of 10 months furnish a basis for rough calculation of the trade for the full fiscal year. They suggest that the exports of raw cotton will aggregate not far from \$600,000,000 in value. Iron and steel manufacturers exported will approximate \$250,000,000; meat and dairy products, \$150,000,000; breadstuffs, \$125,000,000; copper, \$100,000,000; mineral oil, \$100,000,000; wood and manufactures thereof, \$90,000,000; and leather more than \$50,000,000.

The statement of cotton exported for 10 months shows a valuation of \$550,000,000, which is \$143,-

000,000 greater than the corresponding months of 1910. This large value of raw cotton exported, which will be by far the largest total ever reported in any single year, is largely due, officials say, to high prices rather than to large quantities exported.

COMMERCIAL INVESTIGATION OF CHEMICAL INDUSTRY.

Owing to the increasing American interest in the chemical industry of the world, and the desire to secure information concerning its remarkable expansion in Europe, the Bureau of Manufactures is about to undertake a special investigation along these lines. Practical suggestions are invited from the trade as to the most desirable subjects to be taken up, and as to the most promising lines for commercial expansion. The imports of chemical goods and drugs into the United States are reaching enormous proportions, having been \$90,000,000 in value last year, against \$67,000,000 in 1908, while the exportations of chemical products from the United States have remained almost stationary, the aggregate reaching about \$20,000,000 per annum.

The chemical trade is a very broad one, but has special phases well worth study from the commercial aspect. To this end it is thought that correspondence as indicated will prove beneficial.

THE NOBEL PRIZE.

The Nobel prize for chemistry for the year 1910 has been awarded to Professor Wallach, the well-known authority on the essential oils and their constituents. On the occasion of the presentation of the prize Professor Wallach gave an address dealing with the progress of research in the domain of essential oil chemistry, and foreshadowed some prospects of the future development of the science. He urged that the aim of research work should be twofold: the exploitation of the latest synthetic methods, and their application to allied branches of chemical industry, especially in the synthesis of other compounds of similar structure and odor, and also the study of the conditions governing the formation of essential oils in the plant tissues.

ACETYLCELLULOSE FILMS WITHDRAWN FROM THE MARKET.

It appears that the Eastman Kodak Co. which, about two years ago, commenced the introduction of non-inflammable cinematograph films made from acetylcellulose has decided to abandon the manufacture of these films and to go back to the old film made from nitrocellulose. The acetyl films were inferior in lasting qualities to the old films and the general trade objected to their use.

It is claimed that newly invented appliances in the projecting machines will protect the nitro films against catching fire and exploding in case of accidents.

From a technical point of view it is greatly to be regretted that such a retrograde step becomes necessary.

ALASKA GOLD OUTPUT 1909.

In 1880 gold was produced in Alaska to the value of \$20,000. In 1909 the amount mined was valued at more than \$20,000,000. In 1888 silver was first produced in Alaska, to the value of \$2,181; in 1909 the value was \$76,934. In 1902 copper was first produced, to the value of \$41,400; in 1909 its value reached \$536,211. These and other statistics of production are shown by Alfred H. Brooks, of the United States Geological Survey, in "Gold, Silver, Copper, Lead and Zinc in the Western States and Territories," published as a separate chapter of the volume "Mineral Resources of the United States in 1909."

SYNTHETIC CAOUTCHOUC.

By FRANK E. BARROWS, Assistant Examiner, United States Patent Office

Under this title a most comprehensive review of the literature on the subject of the "Synthetic Production and Constitution of Rubber" has been published in the May number of the *Armour Engineer*.

Besides quoting most completely from all publications on this subject and giving especially valuable extracts from the recent articles of the Russian investigator, Lebedeff, the author propounds a most interesting and plausible new theory on the polymerization of diolefins and the formation of rubber. The study of the article is highly recommended to everybody interested in the subject.

GEM IMPORTS.

The imports of precious stones and pearls for May as reported by Francis W. Bird, appraiser of the port, shows that receipts of this character are increasing in value. The value of imports of gems, including pearls, during May was \$2,663,829, compared with \$2,717,082 in May one year ago, and \$2,689,213 two years ago. The invoices and appraisal orders received during May are stated to be 34,162 while in the same month one year ago they were about 1,000 less.

AUTOMATIC GLASS BLOWERS.

In its May issue *The American Flint* states that the Owens Bottle Machine Co. has perfected a machine that produces 10 one-gallon packers per minute, and a machine that makes 47 prescription bottles per minute. It is further stated that the prescription machine is capable of making from 2- to 10-ounce bottles.

GENERAL NOTES.

The United States Civil Service Commission announces the postponement to July 5, 1911, of the examination announced to be held on May 24, 1911, to secure eligibles from which to make certification to fill three or more vacancies in the position of assistant in the paper and textile laboratories of the Bureau of Standards, at salaries ranging from \$900 to \$1,600 per annum.

As an insufficient number of applications were re-

ceived for the examination for this position announced to be held on May 24th, qualified persons are urged to enter this examination.

James Smith, chairman of the manufacturing committee of the Standard Oil Co., died on May 15th in New York City, of apoplexy at the age of 53 years. He had been with the Standard Oil Co. for 38 years. It is said that Mr. Smith was the first man to succeed in refining Texas oil.

The Pelham Phosphate Co., of Pelham, Ga., is erecting a plant for manufacturing acid phosphate and sulphuric acid. The plant will have an annual capacity of 15,000 tons of acid phosphate.

Dr. Edward B. Voorhees, director of the New Jersey Agricultural Experiment Station and Professor of Agriculture at Rutgers College, died on June 6th, of paralysis.

A fire resulting from the explosion of 200 gallons of paint stored in her hold burned the lake passenger steamship *Northwest* at Buffalo, the damage totaling \$500,000.

An anonymous colliery owner through Winston Churchill, British home secretary, offered a prize of \$5,000 for an efficient electric safety lamp.

CONSULAR AND TRADE NOTES.

TEXTILE YARNS AND FABRICS FROM PAPER.

Consul Augustus E. Ingram refers to an interesting paper read at the recent meeting at Manchester of the Textile Institute, by Carl Pontus Hellburg, of Halmsted, Sweden, on *Pine Fiber: A New Fiber for Textile Manufacturing*. Mr. Hellburg, who has studied paper spinning for 10 years, traces the history of this art from the hand-spun paper twines and yarns used years ago in China and Japan to the attempts in the United States some 20 years ago to spin paper yarns for textile purposes.

The manufacture of yarns spun from wood pulp or half-made paper was attempted for many years in Germany, and at Waldhof, near Mannheim, the so-called "Licella yarn" was produced, but the yarn department of these works was closed in 1907-8 in consequence of unsuitable machinery, the high cost of production, and the unsatisfactory strength of the yarn.

A superior pulp yarn called "silvalin" was first made at the Elberfeld paper mill, but in 1909 the works were transferred to Hammern, Rheinland, Germany. The method of production employed, according to Mr. Hellburg, is unsuitable for building up a large industry, there being too much waste and too great a difficulty in keeping the rolls sufficiently moist for a few hours until the spinning process takes place. Therefore, Mr. Hellburg says:

"In order to obtain an absolutely first-class yarn from pine fiber, finished paper made from the very best sulphite or sulphate pulp must be used, this pulp to be made from the slowly growing white pine which is found in Russia, Finland, Sweden, Norway, Canada, and the United States. The spinning of yarn from finished paper gives that yarn a suitable strength. It has also been proved by the trials I have made that Swedish Kraft paper gives a yarn 20-25 per cent. stronger than other kinds of paper."

Putting aside the advantage of obtaining a stronger yarn by using finished paper instead of pulp, there is no saving in producing yarn from the pulp direct, as the pulp, or half-made paper as it should be called, in order to be spun has to be subjected to the same treatment as in making paper, with the exception of the finishing.

Paper yarn for textile purposes, called xylolin, is manufactured in Saxony and Austria, and is used for backing carpets

and for making carpets composed exclusively of paper yarn. [Samples of xylolin are on file at the Bureau of Manufactures.] The cost of production by the Claviez method is rather high, partly because the spinning mills do not make their own raw material—the paper itself; and partly because the machinery employed is not altogether satisfactory. Mr. Hellburg has consequently invented and patented a combined cutting, dividing, and rolling-to-bobbin machine. Mr. Jagenberg, of Dusseldorf, has constructed a ring-spinning machine for paper which works satisfactorily and requires only one employee at each side of the 100-spindle machine as against two for the Claviez machine of 120 spindles. The new method consists of 9 operations as against 102 in the old method.

The appearance and strength of the yarn will depend on the quality of the paper. From Swedish Kraft a very strong yarn is obtained. Pure sulphite paper which is not mixed with mechanical pulp also produces a serviceable yarn, which is good for many purposes. For specially fine yarn tissue paper is the best. At present there is no paper specially made for spinning purposes, and all Mr. Hellburg's trials have been made with common wrapping paper, the results obtained being exceedingly good. So far, coarse counts only have been produced.

Paper intended for spinning should be about 19 inches wide and in rolls; these are placed in the cutting machines, which cut the entire width in one operation in strips of one-sixth to one-half an inch or any required width. The strips thus obtained are simultaneously carried over to the dividing and rolling-to-bobbin machine, and are cut at a speed of about 44 yards per minute. They are separated and rolled on the bobbins in lengths of about 3,000-5,000 yards on each bobbin. These bobbins are then removed to the spinning machines, with one bobbin for each spindle, and the paper strip from each bobbin is carried to a dampening roller, and directly after leaving this roller is spun into yarn on a ring spindle, either upon a wooden bobbin or a conically shaped paper tube. The spinning production averages about 356 pounds per 100 spindles in 10 hours.

With regard to the uses of this paper yarn, packing twine and cord have been made; and samples of these and several other manufactures are forwarded [and will be loaned to interested firms by the Bureau of Manufactures.] Spindle bandings have also been cheaply made and have the additional advantage of

being easily washed without fraying. The cotton of which these bands are usually made could be saved for other purposes.

Carpets of all-paper yarn are already in great demand. In carpet backs the paper yarn is said to be superior to jute yarn. It is also useful for floorcloth for linoleum and in such linen fabrics as paddings, waterproof canvas, scenery cloth, etc., the paper yarn can be used as weft. There are many other fabrics to be made of a union of paper yarn and cotton such as upholstery, cloth, mattress cloth, etc. Trimmings for curtains and furniture have also been made, composed of a paper yarn overspun with silk. Samples of white paper yarn dyed in the hank are also forwarded; to insure thorough penetration of the dye, the dyeing should be effected in the pulp.

As a substitute for jute it may be very welcome for bags, sacks, and packing cloth. For wool packs a cloth of all-paper yarn would be very suitable because of its clean surface; the objectionable presence of vegetable fiber in wool might thus be lessened.

It is claimed that this paper yarn is not damaged by hot or cold water. Paper yarn tarpaulin was alternately boiled, air-dried, immersed in cold water, and ironed without suffering damage. [The full text of the inventor's address on "Pine Fiber for Textile Manufacture" may be obtained from the Bureau of Manufactures.]

NEW METHOD OF WOOD PRESERVATION.

A chemical process for the preservation of wood is described in a report sent to the Bureau of Manufactures by Consul-General William A. Prickitt. A limited company in New Zealand is now engaged in treating chemically lumber of ordinary quality for railroad ties, fence posts, etc., and the claim is made that the material so treated will last as long as the best wood the forests can produce.

The preserving process is said to be simple and inexpensive, and consists essentially in boiling the wood in a saccharine solution to which certain other substances are added according to the special purpose for which the lumber is required. The lumber is not subject to any external pressure or vacuum at any stage of the process. The wood as it is received is immersed in a cold solution in large open tanks. This solution is gradually raised to the boiling point and is maintained at this temperature for a certain time, depending on the size and density of the wood. After cooling, the wood is removed and placed in a drying kiln, the temperature of which is slowly raised. When sufficient desiccation has taken place the kiln is gradually cooled down. The time occupied by the whole treatment generally takes but a few days, though in special cases and for large-sized timber it may be extended for several weeks. The action which takes place is described as follows:

As a saccharine solution boils at a slightly higher temperature than water, the moisture in the wood is converted into vapor and escapes along with the air. During the boiling the albuminous matter in the wood is coagulated and rendered inert. In some measure this coagulation accounts for the strength of the wood being increased by this process. While cooling, the solution is rapidly absorbed by the wood and penetrates every part of it.

The company is executing an order for 180,000 sleepers for the Government Railway Department, and the works were lately inspected by the Prime Minister. The company is also treating large quantities of wood for use in railway cars and carriages.

Among the advantages claimed for this process is the statement that the timber can be treated as soon as it is brought in from the woods and then immediately used for the purposes required, whereas in the ordinary way the timber must be allowed to season before being worked up. It is claimed, also, that there is no waste in lumber which has been treated, as the process stops all warpage and splitting, as well as rendering it absolutely immune from dry rot and borer insects.

CANADA'S ASBESTOS SUPPLY.

According to an official report, Canada produces 82 per cent. of the world's supply of asbestos. The companies operating asbestos quarries and factories in Canada are capitalized at \$24,290,000. In 1880 only 380 tons of asbestos were produced in the Dominion, valued at \$24,700; in 1909 the output was 63,300 tons, valued at \$2,300,000. In 1909 2,000 men were employed in the asbestos industry, and received wages amounting to \$1,350,000. In the Black Lake quarries, in the Province of Quebec, there are 45,000,000 tons of asbestos rock in sight.

The asbestos slate or shingle industry is being developed by the plants in Canada, and predictions are made that in a short time 75 per cent. of all the asbestos produced in the Canadian quarries will be used for asbestos shingles. The asbestos-slate business is only five years old, but during that time the demand for this article has increased enormously, and large factories are being established to supply the demand for this new roofing material.

NATURAL GAS DISCOVERIES IN HUNGARY.

The Hungarian Government has decided to monopolize the tremendous natural gas source recently discovered at Kissarmas, in Transylvania, of which the daily yield amounts to 26,000,000 cubic feet. The gas comes out of the ground at a pressure of over 30 atmospheres, and the noise it makes is heard many miles away. The prices for land in the neighborhood have already increased tenfold, and Kissarmas, from being only a little hamlet lost in the mountains, promises to become a very important industrial center.

The Government engineers estimate that the yield will be sufficient to illuminate all the towns and villages in Transylvania, and also to bring over by pipes large quantities of gas to Budapest. Other borings for gas have already been commenced at Dieso-Szent-Marton, Ura Maros-Szent-Gyorgy, Sachsish-Regen, and Szent-Benedek.

The annual report of an artificial-silk factory near Frankfort shows a clear loss of \$346,052 for 1901. This same company in former years paid as high as 35 per cent. Shares, which at one time brought as high as \$133 on the local stock market, have been as low as \$23 and are now selling at \$30. The price of artificial silk has dropped 60 per cent. in the last few years, being now \$1.20 per pound.

BOOK REVIEWS.

Nitrocellulose Industry. By EDWARD C. WORDEN. Vol. II. Octavo, xxviii, 672 pp., 176 illustrations. D. Van Nostrand Co., New York. 1911. Price, \$5.

The review of the first volume of the "Nitrocellu-

lose Industry" appeared in the June number of THIS JOURNAL. The general criticism of the work there given also applies, for the most part, to the second volume, which includes the following additional sub-

jects: celluloid and the pyroxylin plastics, including a historical account; the compounding, rolling, pressing and sheeting of celluloid; the process of making the various kinds of mottled stock; the fashioning of celluloid into the many articles used in the arts; celluloid substitutes; the analysis of celluloid; and a list of English and United States patents relating to the pyroxylin plastics: the use of cellulose nitrates in microscopy, pharmacy, medicine, and photography; the manufacture of smokeless powder and high explosives, with description of the various forms prepared for the trade and the more important stability tests; the manufacture and uses of cellulose acetate and viscose; United States regulations for the use of denatured alcohol; appendix including patent, name and subject index.

In treating the above subjects the author has laid special stress on the pyroxylin plastics, the chapter on this subject being really a book in itself. In it are included descriptions of nearly all the important processes used in the manufacture of celluloid, gathered from a careful search of the patents and literature and from personal contact during many years with those engaged in the industry. The account differs favorably from that appearing in a recent work on celluloid by giving the preponderance of space and emphasis to the preparation of celluloid from the raw materials instead of to the fashioning of the finished product. The author has included in this account a great many obsolete or impracticable processes, intentionally for the sake of completeness, as explained in the preface, but in many cases without indicating either by order of presentation or otherwise which are the essential and which the non-essential facts. For example, there are a number of descriptions of processes proposed or patented by J. Edson, a man who did not make a success of the celluloid business and went into a different line of work many years before his death.

The chapter on the use of cellulose nitrates in photographic films contains a great deal of interesting information but the author often wanders far from his subject and writes much that might better be included in a treatise on photography.

"Guncotton, Smokeless Powder and Explosive Cellulose Nitrates." opens with the statement that the subject matter is incomplete as compared with the other sections of the work, the object being to record the more important facts. It is unfortunate that the other sections were not written with this same object for here one may readily get at the essential operations, the descriptions of which are accompanied by reproductions of photographs taken from a large plant. More specific descriptions are given in notes in finer print and the general arrangement of the chapter is excellent. The reader is enabled to learn the steps necessary to produce the finished explosive and to obtain a good idea of the different types now in use. This has been accomplished without sacrificing the author's object stated in the preface, of not having the text leave off at just that point where specific information is most desired.

Cellulose acetates are described from a chemical as well as technical point of view and a translation is given of a notable contribution to the subject by C. G. S. Schwalbe. Here, as in the rest of the work, the information has been brought up to date in a manner unusual in a book of this kind.

The above subject as well as the chapters on viscose and denatured alcohol which follow are out of place in a book on the "Nitrocellulose Industry," but their presence may be pardoned on the ground that the work is probably destined to reach many small libraries where it will form a comprehensive and valuable addition.

C. M. JOYCE.

The Iron Ores of Lake Superior. Containing Some Facts of Interest Relating to Mining and Shipping of the Ore and Location of Principal Mines, with Original Maps of the Ranges. By CRAWELL AND MURRAY. Chemists and Metallurgists. Cleveland, Ohio. The Penton Publishing Co., Cleveland.

The book opens with a short history of the Lake Superior district, stating that iron ore was first discovered in Michigan in 1844. First iron made in an old forge on Carp River 5 miles east of Negaunee, February 10, 1848. First shipment of ore from Lake Superior region was made July 7, 1852, six barrels being the consignment. First ship canal around the rapids at Sault Ste. Marie was completed in 1855—regular shipments by boat in 1856.

The geology of the region is given, briefly outlining the important features in the various ore-bearing districts. Eight pages are devoted to mining methods, transportation and classification of ores.

The method of sampling ores adopted by the Independent Chemists of Cleveland is given in full, followed by methods of analysis that are in general use.

One hundred and forty pages are devoted to descriptions of 365 mines, this including nearly all of the mines on the different ranges. This description gives location, date opening of mine, nature of the ore, system of mining, greatest vertical depth of mine, road over which ore is shipped from mine, sales agent, yearly shipments, total tons shipped, and average analysis dried and natural of ore shipped for the season of 1910.

As stated in the preface, much of the information contained in the book has appeared in the various trade journals, geological reports and scientific society transactions.

The authors have, however, compiled these scattered facts and presented this information in a very acceptable and concrete form. To this they have added, as stated above, a late description of most of the mines on the different ranges and have worked out maps showing their exact location.

To any one desiring information relative to the iron ores of Lake Superior, I would recommend this book.

WILLIAM BRADY.

"The Chemistry of Coal Tar Dyes." By IRVING W. FAY. D. Van Nostrand Co., New York. 1911. 365 pages; \$4.00 net.

This volume is an attempt to develop in a somewhat systematic manner the chemistry of the more important coal tar dyes. The author has succeeded in

making a book which will, without doubt, prove interesting to the student of dyestuffs, though it will require considerable previous knowledge of organic chemistry to appreciate the large amount of theoretical chemistry contained in this book. In fact, the author has concerned himself principally with the theory of the subject, chiefly with the idea, it would seem, of describing the structural formulas of the various dyestuffs. Though the book will be of value to the student as an amplified chapter in general organic chemistry, it cannot be of much use to the practical dyer, who would only be utterly dumbfounded by the array of complicated structural formulas, presented and who would look in vain for any proper technical matter relating to the properties and methods of application of the various dyestuffs described.

Unfortunately, the value of this book as a contribution to scientific literature is greatly marred by various crudities of style and diction. As a whole, the material appears to be rather slovenly and uncritically thrown together. The sentence, for instance, on page 5, commencing "If coal be heated equally hot," reminds one unfortunately of Freshman attempts in prose composition. Under the description of nitrobenzene we find the following: "In commerce it is known as 'nitrobenzole for blue' or 'nitro benzole for red,' the first is principally used in the manufacture of aniline for blue; the latter is used for preparing aniline for reagents." There is nothing to indicate to the reader the difference which must exist in these two varieties of nitrobenzene. "Piesic acid is the final oxidation product of many aromatic substances" is an inaccurate statement. In speaking of naphthol yellow the author writes: "On account of the sulpho group, which this possesses over Martins yellow, it is a more valuable dye. It is more soluble and acids cause no precipitate in its yellow solution." This would lead us to infer that acids would cause a precipitate if its solution were some other color. These examples of bad styles occur scattered generally throughout the entire book, and detract a great deal from the reader's appreciation of its otherwise many good qualities. In this connection we cannot help quoting one of the early sentences in the book, which surely must be a literal translation of a German original, for we cannot conceive of an American mind of itself ascending to such heights of literary

structure: "From the early manufacture, of a nature so crude that during suits, in Paris in the early days, of one manufacture against another for infringements of patents neither counsel nor experts could either dispute or establish the identity of products made by different oxidizing agents upon the same raw materials, to the present day, when research is often able to reveal the actual structure and how the complex dye molecule is built up, is a long history of processes which have been improved by a most persistent and thorough study, both theoretical and practical, by the celebrated investigators of the scientific world." Truly wonderful!

This book also exhibits careless inconsistencies in spelling the same word, such as "alizarine and alizarin," "chromophor and chromophore," "amido and amino." The author probably means "generic" when he speaks of "the genetic relation." In writing of the substantive cotton dyes on page 142, he calls them "dye salts" when he should have said "salt dyes." In the chapter on triphenylmethane dyes, the page heading "triphenylmethane" is misspelled three times in the space of a few pages, and there are numerous other evidences of careless proof-reading. In the section on "ingrain colors" (which by the way is an obsolete term), the author seems unaware of the existence of primuline, which is the most widely known and extensively used of this group of dyes. Also, the new and very important, as well as very highly interesting, group of vat dyes is not mentioned, with the exception of credigo and a few indigo products. The author is apparently ignorant of the indanthrene dyes, and the other groups of dyes of this same nature. The chapter on sulphur dyes is also very out-of-date, and does not at all represent the condition of the science at the present time, and most of the products treated are now unimportant or totally obsolete. In the chapter on mordants, the author unfortunately has gotten hold of some very archaic matter. The description of mordanting cotton with alum (on page 401) reads almost like an extract from a mediæval book on dyeing, especially the last sentence: "The cotton is then washed without losing what it has gained by this treatment and the now mordanted fiber will absorb the various shades of color and hold them securely, beyond the power of water to remove."

J. MERRITT MATTHEWS.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

Quartz-glass: Its History, Manufacture and Uses. By P. GUENTHER. 8vo., 52 pp. Berlin. (German.)

The Chemistry of Honey. By O. HAENLE. 4th Edition. L. 8vo., 80 pp. \$1.25. Strassburg. (German.)

Directory of American Gas Companies—1911. By E. C. BROWN. 8vo., 641 pp. \$5. Press of Progressive Age, New York.

Engineering Chemistry. By THOMAS B. STILLMAN. 4th Edition. 8vo., 744 pp. \$5. The Chemical Publishing Co., Easton.

Chemist's Pocket Manual. By RICHARD K. MEADE. 2nd

Edition. 8vo., 544 pp. \$3. The Chemical Publishing Co., Easton.

Directory of the Entire Glass Industry of Europe. Vol. I. Germany, 1911. No author. Sm. 8vo. 295 pp. \$1.25. Schulze & Co., Leipzig. (German.)

Transformer: A Treatise on the Theory, Construction, Design, etc. By H. BOHLE AND D. ROBERTSON. 8vo., 370 pp. \$5.25. C. Griffin, London.

Modern Explosives. By P. F. CHALON. 3rd Edition. 8vo., \$5. Ch. Béranger, Paris.

- Short Textbook of Radioactivity. By P. GRUENER. 2nd Edition. L. 8vo., 119 pp. 75c. A. Franke, Bern. (German)
- General Agricultural Chemistry. By E. B. HART AND W. E. TOTTINGHAM. 120, 334 pp. \$1.50. Privately printed (E. B. HART), Madison, Wisc.
- Transportation of Gases, Liquids and Solids. By OSKAR NAGEL. 8vo., 200 pp. \$2.50. Vacher & Sons, London.
- Physico Chemical Tables. Vol. II. Physical and Analytical Chemistry. By CASTELL-EVANS. 1220 pp. \$12. J. B. Lippincott Co.
- Dictionary of Electrical Engineering. By HOBART. 2 Vols. \$10. J. B. Lippincott Co.
- Methods of Modern Sewage Purification. By G. BERTRAM KERSHAW. 340 pp. \$7.50. J. B. Lippincott Co.
- Alchemy: Ancient and Modern. By H. STANLEY REDGROVE. \$1.25. Wm. Rider & Son, London.
- Acetylene: Its Properties, Generation and Uses. By J. H. VOGEL. 8vo. \$4. O. Spamer, Leipzig. (German.)
- Chemical Technology of Paper. By G. DALÉN. 120 pp. \$1. J. A. Barth, Leipzig. (German.)
- Chemical Technology of Glass. By BERNHARD MUELLER. 103 pp. 50c. J. A. Barth, Leipzig. (German.)
- Chemical Technology of Leather. By JOHANNES PAESSLER. 18 pp. 50c. J. A. Barth, Leipzig. (German.)
- Chemical Technology of the Fats, Oils and Waxes. By C. STIEPEL. 146 pp. \$1.25. J. A. Barth, Leipzig. (German.)
- Rubber and Its Examination. By F. W. HINRICHSSEN AND K. MEMMLER. 254 pp. \$2.25. S. Hirzel, Leipzig. (German.)
- Chemical-technical Lexicon. By JOSEPH BERSCH. 2nd Edition. \$4.50. A. Hartleben, Leipzig. (German.)
- Essential Oils: Semi-annual Report of Schimmel & Co., April 11. Schimmel & Co., Miltitz. (German and English.)
- The Fats. By J. B. LEATHES. 138 pp. \$1.20. Longmans, Green & Co., New York.
- The Rubber Country of the Amazon. By HENRY C. PEARSON. 8vo., 250 pp. \$3. India Rubber Publishing Co., New York.
- Elements of the Metallurgy of Iron. By T. GEELINKIRCHEN. Vol I., 8vo. \$2. J. Springer, Berlin. (German.)
- Gmelin and Kraut's Handbook of Inorganic Chemistry. 7th Edition. Zinc, Cadmium and Indium. By W. ROTH. Vol. IV, Part 1. L. 8vo., 1056 pp. \$11. Heidelberg. 1911. (German.)
- Gmelin and Kraut's Handbook of Inorganic Chemistry. 7th Edition. Phosphorus, Boron and Carbon. By GUTBIER. Vol. IV, part 3. L. 8vo., 907 pp. \$9. Heidelberg. 1911. (German.)
- Treatise on Inorganic Analysis. By A. CARNOT. Vol. III. 8vo. \$5.50. Paris. 1911. (French.)
- Yearbook of Organic Chemistry. By J. SCHMIDT. Vol. IV. for 1910. L. 8vo. \$4. Ferdinand Enke, Stuttgart. (German.)
- Sulfur Tars: Their Production and Treatment. By W. SCHEITHAUER. 8vo. \$2.50. O. Spamer, Leipzig. (German.)
- Chemical Technical Methods of Analysis. By GEORG LUNGE AND ERNST BERL. 6th Edition. Vol. III. 8vo., 1044 pp. \$6. Julius Springer, Berlin. (German.)
- Electrically Controlled Constant Temperature Water Bath for the Immersion Refractometer. By H. C. GORE. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular No. 72.
- Enological Studies. By WM. B. ALWOOD. U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin, No. 140.

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

- Manufacture and Properties of Hydrated Lime. By RICHARD K. MEADE. *Engineering News*, May 11, 1911, pages 554-559.
- Analysis of Crude Glycerin. By W. GRUENEWALD. *Zeitschrift fuer angewandte Chemie*, xxiv, No. 19, pp. 865-870. (German.)
- Physical and Chemical Properties of Portland Cement. By W. C. REIBLING AND F. D. REYES. *Philippine Journal of Science*, A, Vol. V., No. 6, pp. 367-417.
- Natural Dyes and Coloring Matters of the Philippines. By B. T. BROOKS. *Philippine Journal of Science*, A, Vol. V., No. 6, pp. 439-452.
- Some Experiments Relating to Hops and Yeast. By HAROLD W. HARMON. *Journal of the Institute of Brewing*, Vol. XVII, No. 4, pp. 359-383.
- Raw and Pasteurized Milk and Milk Serums. By EDWARD GUDEMAN. *Illinois Medical Journal*, April, 1911.
- The Role of Slag in our Metallurgical Processes. By CARL DICHMANN. *Stahl und Eisen*, May 11, 1911, pp. 749-759. (German.)
- Significance of Lead Arsenate Composition. By W. H. VOLCK. *Science*, June 2, 1911, pp. 866-870.
- A Plea for the Use of References and Accuracy Therein. By F. ALEX. McDERMOTT. *Science*, June 2, 1911, pp. 852-853.
- Nature of the Combination between Fiber and Dye. By JEROME ALEXANDER. *Journal of the Society of Chemical Industry*, Vol. XXX, No. 9, pp. 517-518.
- Viscosity of Nitrocellulose Solutions. By C. PIEST. *Zeitschrift fuer angewandte Chemie*, 1911, Heft 21, pp. 968-972. (German.)
- Asbestos as a Commercial Product. ANONYMOUS. *India Rubber World*, Vol. XLIV, No. 1, pp. 235-236.

RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

987,850. Process of Treating Ores.

This is a process for treating metalliferous ores, particularly those bearing the more valuable metals, such as gold, silver copper, etc., and the invention resides in taking uncrushed ores as they come from the mines or after they have passed through the primary breakers and alternately lifting and dropping the same onto a hard surface or surfaces within a container whereby to pulverize the ores, and while dropping subjecting such ores to a high temperature by dry heat to drive off the water of crystallization and volatile products in the ore and render the ore mass spongy and cause the same to decrepitate, thereby assisting

in breaking and crushing the ore on impacting with the hard breaker body so as to pulverize the ore.

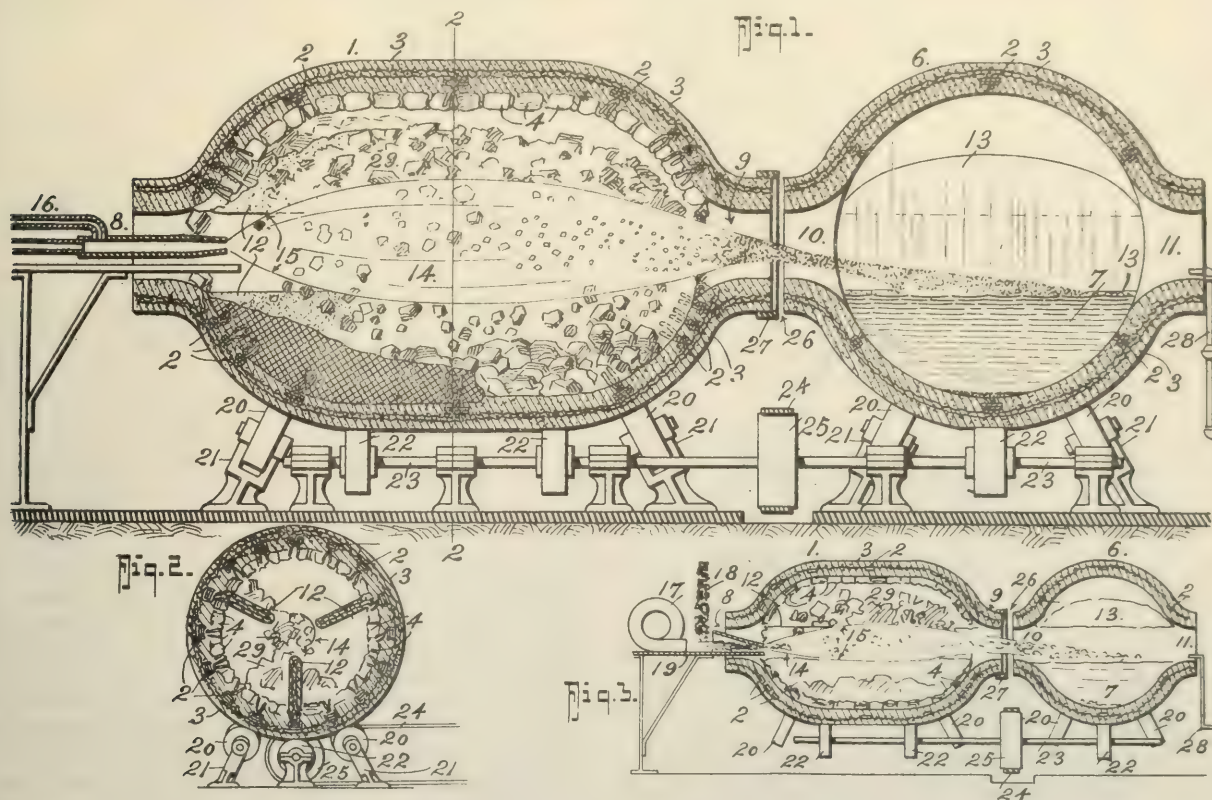
In the use of the apparatus shown in the accompanying illustration, the ore 29 to be treated is placed in the container 1 and the fuel for heating is also introduced when the oil burner 16 is used to produce the heat blast from inlet to outlet of the container 1. Having introduced the ore in large chunks as it comes from the mine (or after it has passed through the first breakers) into the container 1 and having introduced the solvent into the container 6 (the solvent being a cyanid or other solution when gold and silver ores are undergoing treatment) a hot blast is

produced by igniting the burner 16 in any desired manner, and the containers are set in motion. The ore 29 will be carried up by the partitions 12 and 13 and dropped through the blast or flame 15 where they will come into direct contact with the hot blast and have their water of crystallization and volatile products driven off. Any sulphur in the ore will be removed in this manner. The ore having dropped through the hot blast 15 impacts the crusher surface 4 of the container at the bottom and inasmuch as the structure of the ore in being heated is weakened and made porous, the impact will break and crush the ore, which breaking and crushing is further assisted by the rolling and tumbling of the softer particles in connection with the

practically so, so as to avoid the boiling of the solvent but still allow sufficient heat to assist the chemical reaction.

As soon as a sufficient quantity of ore is deposited in the solution 7 in the container 6, said container is rolled away and another container substituted. The dissolved ore and solvent from the container 6 which has been rolled away may be emptied after forced percolation by steam or vacuum, or both, and extracting the values thereby into any suitable reservoir where it may be further treated by the usual means to separate the dissolved values if any remain.

The inventor is Isaac A. Braddock, of Haddonfield, New Jersey, assignor of one-sixth to William C. Cood, of Baltimore



harder particles in the container 1 during its rotation. The temperature within the container 1 is usually carried up to about 500° F. so as to thoroughly dry the ore and drive off the volatile products.

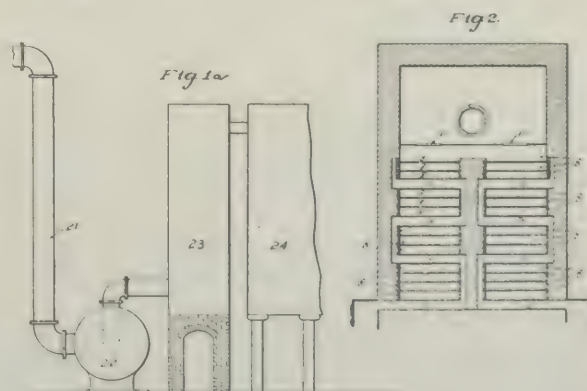
Attention is called to the fact that the removal of the volatile products in the ore while passing through the heat zone causes decrepitation to take place, and the ore becomes porous and spongy so when it contacts the bottom of the container it will be broken and crumbled, the breaking and crumbling action being also assisted by the rolling and tumbling of the ore within the retort during its movements, the heavier and lesser heated ores serving to assist in crushing the softer particles until the ore is reduced to a fine powder. The force of the heated blast serves to cause the crushed particles of the ore to gradually work toward the outlet 9 of the container and as soon as the ore rocks have been crushed fine enough the heated blast will carry the ore particles through the outlet 9 of the retort 1 into the second container 6 where the hot ore particles are deposited into the solvent 7. The container 6 being provided with partitions 13 will serve to agitate the solution within the container 6 and as the hot ore particles are directly deposited into said solution the temperature within the container 6 will be maintained at the desired degree (usually from 200° to 212° F.). The air opening between the containers 1 and 6 is so regulated that the temperature within the container 6 will be maintained constant or

Maryland, and one-sixth to Nicholas A. Kestler and one-sixth to David E. Anthony, of Washington, District of Columbia.

988,646. Process of Making Sulfuric Anhydrid.

This invention relates to a process of manufacturing sulfuric anhydrid from iron and copper pyrites, sulfid ores, and mattes resulting from the treatment of such ores.

In carrying out the process, sulfur-bearing ores or mattes, preferably fines, on account of their lower commercial value,



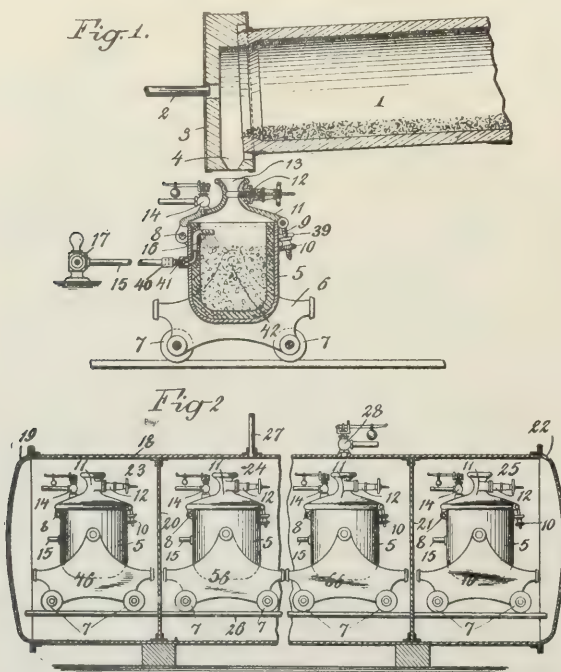
are ground to an impalpable powder. This is then fed into a furnace, kiln or shaft, heated to a temperature high enough to ignite the sulfur, preferably being fed by an air blast or drawn into the furnace by a fan or blower suction. The pulverulent ore is at once ignited, with formation of sulfurous anhydrid and metallic oxids. The finely divided metallic oxids are carried along in the furnace with the mixture of sulfurous anhydrid and air, and being in such a fine state of division, act at once as a catalyzer, converting 30-40 per cent. of the sulfurous anhydrid into sulfuric anhydrid, and at the same time the gases are purified by the removal of arsenic and the like by their intimate contact with the fine non-volatile oxids. The spent metallic oxids are then separated from the gas. The resulting sulfuric anhydrid is absorbed in strong sulfuric acid in the well-known absorption towers, and the remaining sulfurous anhydrid converted into sulfuric anhydrid by the continuance of the contact process or into hydrated sulfuric acid by the well-known chamber process.

The accompanying illustration shows the apparatus in which the process is carried out.

The inventor is Jos. McPetridge, of Vandergrift, Pa.

988,724. Cement Treating Process.

This invention is a process for treating Portland cement clinker, by running the intensely heated clinker from a rotary kiln into a receiver and treating the same for the desired time with steam at high pressure generated by spraying water upon the heated material in a closed receiver or otherwise, so that the



clinker is disintegrated or made friable so as to facilitate grinding and its ageing or hydration to the desired extent is effected, that is, the free or objectionably loosely combined or lime magnesia in the clinker is hydrated or reduced to other forms.

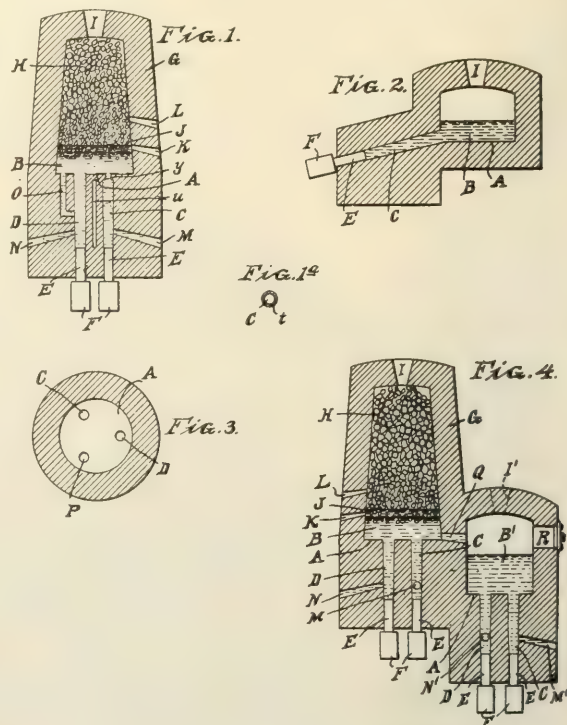
The accompanying illustration shows apparatus for carrying out this process.

The inventors are Robert W. Lesley, of Haverford, and Henry S. Spackman, of Ardmore, Pennsylvania.

988,936. Electric Furnace Process and Electric Furnace.

This invention resides in an electric furnace wherein the resister comprises a column or columns of molten material, electrodes furnishing communication with the columns, the

heat in the column resister being communicated to the main body or mass of molten or other material under treatment by conduction from such resister and chiefly by convection and rapid circulation; and it is a further feature of the invention that the patentee so constructs and proportions the column



resister that the "pinch effect" in such column is availed of for causing more or less violent circulation and movement of the heated material from the columns into the mass of molten material under treatment.

The accompanying illustration is a vertical sectional view of an electric furnace in which the resister is in the form of a column or columns of molten material contacting with the electrodes and communicating with the main mass of molten material above it.

The inventor is Carl Hering, of Philadelphia, Pa.

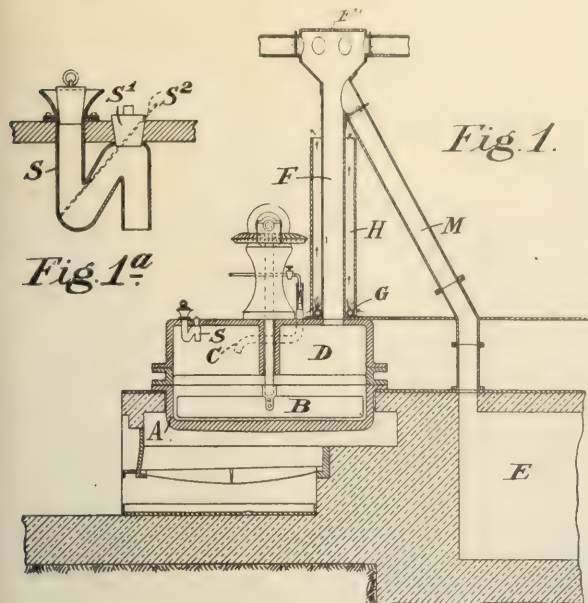
988,963. Manufacture of Lead Oxid and White Lead.

In the manufacture of white lead from oxid by dissolving the latter in acetate of lead solution, nearly half the lead remains behind as sludge. This is owing to the oxid of lead having been fused in its manufacture, and no matter how finely it is ground afterward, this fused oxid is in large part insoluble in the acetate of lead solution.

It is the purpose of this invention to avoid the fusing of the oxid altogether by making it as a highly soluble massicot at a temperature a long way below the fusing point, and thus the difficulty hitherto experienced in working commercial litharge is avoided. Further, in the manufacture of red lead it is also very desirable to have the lead oxid in as fine a state of division as possible to avoid the fusing of the oxid, and to have every particle of the charge at the same degree of oxidation, and especially to avoid powdered lead in the charge, as the lead takes much longer to oxidize to red lead than the fused oxid, and the fused oxid much longer than the finely divided unfused oxid. It is thus impossible to bring all the lead oxid at the same time to the right color, and individual parts are too much oxidized, and others too little.

The process is defined in the patent as consisting in subjecting metallic lead to a blast of air and steam, discharging the mixed

dust and gases in an upward direction, and at the same time heating said dust and gases to a degree slightly below that



necessary to fuse the oxid until the entire lead contents are converted into oxid.

The accompanying illustration shows apparatus in which the process may be carried out.

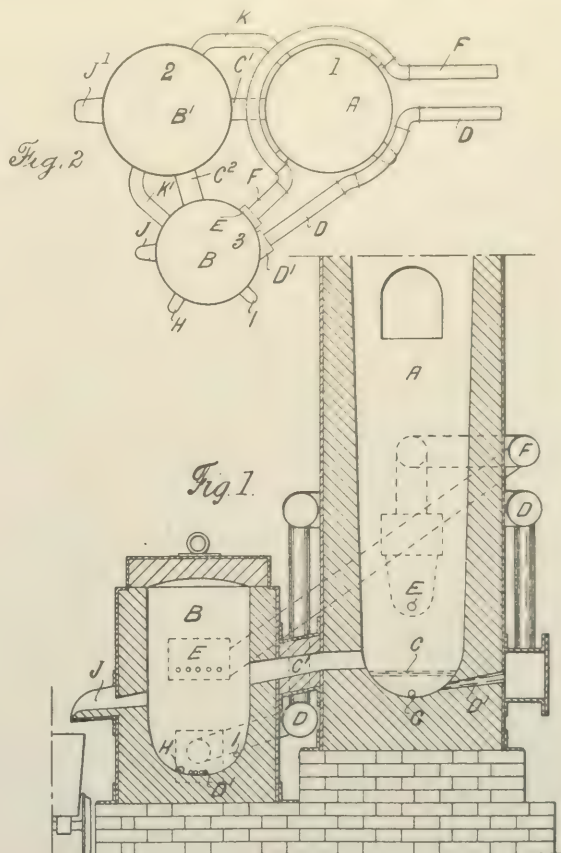
The inventor is George Vincent, of Liverpool, England.

990,266. Manufacture of Steel.

This invention relates to the conversion of iron into steel by a process analogous to the Bessemer method and has more particular reference to improvements in what may be termed the continuous conversion process. In this last-named method the converter is of a stationary type, erected adjacent to or even as part of the cupola, whereby molten cast iron, the product of the cupola, is allowed to pass directly from the cupola hearth continuously into the converter through a conduit or connecting passage. The metal accumulates in the converter, to which blast, under suitable pressure is applied, causing the carbon, and other metalloids to be oxidized and the heated products of combustion to pass up into the cupola and assist in the reduction and melting of the metal. Thus the process of smelting and converting are carried on simultaneously, the bath of molten steel being constantly fuel enriched by passing over of highly carbonized iron from the cupola, and a sufficiently high temperature maintained to insure the combination of the oxygen in the blast with the carbon of the metal, the converter hearth being tapped intermittently for steel, as the molten metal accumulates and gets deprived of its carbon and other metalloids by the action of the air blast. Hitherto in this method of manufacturing steel, there has been excessive slagging, from the converter and the too free passage of molten metal intermingled with slag from the converter resulting in abnormal losses of metal that pass out with the slag while the

converter is in blast. Further, owing to the fact that an ordinary charge such as may be used for this process frequently consists of pig iron, steel scrap, and wrought iron, there is a lack of uniformity in the metal passing into the converter, and the steel is difficult to grade.

Now the object of the present invention is to obtain a purer and more uniform quality of steel. For this purpose there is formed a bath or well at the bottom of the cupola in which the molten metal accumulates and from which it overflows into the converter attached. This bath is supplied with tuyeres similar to those in the converter in order to thoroughly agitate and mix the molten metal, and remove by oxidation any excess of



silicon, manganese or other impurities in the metal before it overflows into the said converter. The presence of the coke in the cupola bath prevents any appreciable reduction in the quantity of carbon in the metal, so that the metal overflowing into the converter does not contain more silicon and manganese than is required to be removed before the carbon is reduced to the desired percentage, but if found necessary carbon may be added in any convenient way to the converter or the bath to make up any deficiency.

The accompanying illustration shows apparatus in which the process is carried out.

The inventor is Thomas James Heskett, of Westminster, London, England.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF JUNE.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Aetancilid.....Lb.	20 ¹ / ₂ @	23
Acetone (drums).....Lb.	13 ¹ / ₈ @	16 ² / ₃
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	2.40 @	2.50
Acetic Acid.....C.	1.58 @	1.73
Aniline Oil.....Lb.	11 ¹ / ₂ @	11 ³ / ₄
Benzoic Acid.....Oz.	11 ¹ / ₄ @	12
Carbon Tetrachloride (in drums).....Lb.	8 @	12
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (in drums).....Lb.	10 @	11
Citric Acid (domestic).....Lb.	38 ¹ / ₂ @	39
Camphor (refined in bulk).....Lb.	46 ¹ / ₂ @	47 ¹ / ₂
Dextrine (imported potato).....Lb.	5 ¹ / ₂ @	7
Dextrine (domestic corn).....C.	2.42 @	2.63
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 ¹ / ₂ @	9 ¹ / ₂
Glycerine (dynamite).....Lb.	21 ¹ / ₂ @	22 ¹ / ₂
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7 ¹ / ₈ @	7 ³ / ₄
Pyrogallie Acid (bulk).....Lb.	1.16 ² / ₃ @	1.38 ¹ / ₂
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	1.67 @	1.83
Starch (potato).....Lb.	4 ¹ / ₄ @	4 ⁵ / ₈
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 ⁷ / ₈ @	5 ³ / ₄
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	30 ¹ / ₄ @	30 ³ / ₄

Inorganic Chemicals.

Acetate of Lime (gray).....C.	1.75 @	1.80
Acetate of Lead (brown, broken).....Lb.	7 ³ / ₄ @	8
Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (in drums) 16°.....Lb.	2 ³ / ₄ @	3
Ammonium Chloride, gray.....Lb.	5 ³ / ₄ @	6
Arsenic, white.....Lb.	1 ³ / ₄ @	2 ³ / ₄
Ammonium Carbonate, domestic.....Lb.	8 @	8 ³ / ₈
Aluminum Sulphate.....Lb.	90 @	1 ³ / ₄
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 ³ / ₄
Barium Nitrate.....Lb.	5 ¹ / ₂ @	6 ¹ / ₂
Borax, crystals in bags.....Lb.	3 ¹ / ₂ @	4
Boric Acid, crystals.....Lb.	7 @	7 ¹ / ₂
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.17 ¹ / ₂ @	1.25
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	90 @	92
Chalk (light precipitated).....Lb.	4 ¹ / ₂ @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (in bags).....C.	60 @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 @	8 ¹ / ₂
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	81 @	84
Nitric Acid, 36°.....Lb.	3 ⁷ / ₈ @	4 ¹ / ₄
Nitric Acid, 42°.....Lb.	4 ⁷ / ₈ @	5 ¹ / ₂
Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25

Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 ³ / ₈ @	11
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals.....Lb.	8 ¹ / ₄ @	9 ¹ / ₂
Potassium Nitrate (crude).....Lb.	4 ³ / ₄ @	5
Potassium Bichromate, 50°.....Lb.	7 ³ / ₈ @	7 ³ / ₄
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	63 ¹ / ₃ @	65 ¹ / ₃
Salt Cake (glass-makers).....Lb.	62 ¹ / ₂ @	77 ¹ / ₂
Silver Nitrate.....Oz.	34 @	36
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 ¹ / ₄ @	5
Sodium Chlorate.....Lb.	8 ¹ / ₄ @	9 ¹ / ₄
Sodium Bicarbonate (English).....Lb.	2 ³ / ₄ @	3
Sodium Bichromate.....Lb.	5 ⁵ / ₈ @	5 ³ / ₄
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 ¹ / ₂
Sodium Hydroxide, 60 per cent.....C.	1.80 @	1.85
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.	6 ⁷ / ₈ @	7
Sodium Nitrate, 95 per cent., spot... C.	— @	2.12 ¹ / ₂
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 ³ / ₄ @	10
Strontium Nitrate.....Lb.	7 ¹ / ₄ @	8
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	86 ² / ₃ @	1.00
Talc (American).....Ton	15.00 @	25.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	12 ¹ / ₂ @	12 ⁵ / ₈
Tin Oxide.....Lb.	49 ¹ / ₃ @	51 ² / ₃
Tin Chloride (36°).....Lb.	11 @	11 ¹ / ₂
Zinc Chloride (granulated).....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Zinc Sulphate.....Lb.	2 ¹ / ₄ @	2 ¹ / ₂

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 ¹ / ₂
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	9 @	20
Corn Oil.....C.	5.93 ¹ / ₃ @	5.98 ¹ / ₃
Cottonseed Oil (crude), f. o. b. mill...Gal.	40 ⁵ / ₆ @	41 ² / ₃
Cylinder Oil (light, filtered).....Gal.	19 ¹ / ₂ @	20
Japan Wax.....Lb.	9 @	9 ¹ / ₄
Lard Oil (prime winter).....Gal.	78 ¹ / ₃ @	85
Linseed Oil (raw, city).....Gal.	88 ¹ / ₃ @	89 ¹ / ₃
Linseed Oil (double-boiled).....Gal.	90 @	91 ¹ / ₂
Paraffine Oil (high viscosity).....Gal.	23 ¹ / ₂ @	24
Paraffine (crude 120 @ 122 m. p.).....Lb.	3 @	3 ¹ / ₄
Paraffine (refined, domestic) 120 @ 122 m. p.....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Rosin Oil (first run).....Gal.	— @	37
Spindle Oil, No. 1.....Gal.	14 @	14 ¹ / ₂
Stearic Acid (double-pressed).....Lb.	9 ¹ / ₄ @	9 ³ / ₄
Sperm Oil (bleached winter) 38°.....Gal.	82 @	85
Tallow (acidless).....Gal.	64 @	66
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum [No. 1 ingots].....Lb.	19 ³ / ₄ @	20 ¹ / ₄
Antimony.....Lb.	— @	9
Bismuth.....Lb.	— @	1.80
Copper (electrolytic).....Lb.	— @	12 ¹ / ₂
Copper (lake).....Lb.	12 ¹ / ₂ @	13
Lead.....Lb.	4.40 @	4.42 ¹ / ₂
Mercury.....Lb.	61.3 @	61.5
Nickel.....Lb.	40 @	50
Platinum (refined).....Oz.	42.50 @	43.00
Silver.....Oz.	— @	53
Tin.....Lb.	— @	45 ³ / ₈
Zinc.....Lb.	5.45 @	5.50

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EDITORIALS.

THE ENDOWMENT FUND.

I use the word "the" as though the visions of Chairman Hyde, indicated by the insert in the June number, were already realized. Like Crockett's coon, the aiming of a gun when a good man's behind it, is almost the same as having hit the mark already.

In the minds of all good members of the Society, there is a more or less well-defined spirit of altruism. The willingness to help is prevalent. This common feeling is certainly developing with rapidity in our country-at-large. In spite of the criticism of a few apparently short-sighted people and of conservatives who ask, "What has posterity done for us, that we should plan and spend for it?" we find all sorts of efforts being expended for the general, as distinct from the individual good. The term "conservation of natural resources" is rapidly becoming an activity. It is a moving force which acts not as the exceptional idea of a single able enthusiast, but as an advance for which our time is ripe. A few seem to fear what they call paternalism, but this name less perfectly fits the case than fraternalism, against which fewer could scoff. Our very laws are many of them founded upon the same fraternalism. Our factory laws, the pure food law, etc., stand for the wish that every one should be assisted in his life, liberty, and pursuit. A federal department devoted to the instruction of mining engineers and miners in the safer execution of their work is not alone a monument to the peculiar foresight and ability of a single man, however much he may have developed the idea. He was not separated from his environment. The work was largely a growth of the times. It is an indicator like the wind-indicating straw. How far the principle may develop, not even the most visionary can imagine. So long as it calls for more life, more effort, more hope, it seems reasonable. When, if ever, it merely reduces for the individual the call for his efforts, instead of substituting needs calling for greater total efficiency in living, then the years of the lean kine will arrive. Paternalism might do this. And this leads to the subject of our Endowment.

An endowment controlled by the American Chemical Society could do a great deal of good. According to the Constitution of the Society, we stand for "the advancement of chemistry and the promotion of chemical research." This is really quite distinct from the advancement of certain chemists and their promotion. An artificial help to the latter might cripple some of them, but any amount of help to the science will only enable the chemists to more efficiently help themselves and the rest of mankind.

Many men who are connected with manufacturing

find themselves in contact with new materials, with physical, chemical and electrical phenomena, with which they, and possibly others, are not familiar. The necessary work of discovery is undertaken after the available knowledge is utilized. This individual research, which discloses necessary and always some unnecessary facts, often remains solely the property of the discoverer. It usually has an intrinsic value because of this fact. The more knowledge we have available, the better, and this applies to the industries and to the individual chemist. It is along this line that I believe in the power and utility of an endowment. It is that our stock of general knowledge may be increased.

Consider examples a moment. A couple of men working for a prize discovered and disclosed the law that permits all of us to know and always remember the approximate specific heats of elements and even solid compounds. Thousands of men have made good use of this law. Countless time has been saved to investigators in this way. Imagine the increase in the rapidity of an advance if we knew the laws governing the hardness, the ductility, the tensile strength, the expansion coefficient, etc., etc., of metal mixtures, especially if these were simply related to some other known properties.

A number of chemists have advanced a little way along the road of agricultural chemistry. It is public knowledge that plants need potash, nitrogen, phosphorus, etc., but the crops of the farmer who places more reliance on the common chemical knowledge than on the old barnyard manure can scarcely be considered hardy. Certainly this condition will improve, but the speed would be greater if facts were collected faster.

There are a great many laws, principles and facts in chemistry the discovery of which seem particularly fitting to our teaching laboratories. The discoveries of the fundamentals of our industries usually originate there. It is there, too, that financial help is most needed. When discoveries assist solely a single industry, it seems fair to expect the industry to bear the cost, but all chemists and manufacturers may share in the product of general chemical research such as the universities of the world are producing. In general, one would apparently not be far wrong who said, let us raise an endowment fund to help young chemists to advance themselves and their science by carrying out research work for publication under the guidance of our good teachers. W. R. WHITNEY.

PURE DRUGS AND MEDICINES.

The protection of the public is amply provided for through our national codex, the United States Pharmacopoeia, which defines the standards of purity and quality of most medicines and chemicals used in compounding prescriptions. This U. S. Pharmacopoeia is the standard accepted by our National Food and Drug Law. It is also the standard adhered to by all conscientious pharmacists and manufacturing chemists.

Upon the request of the "New York World," the

writer undertook the analysis of about 230 prescriptions compounded in various pharmacies located in New York City. The prescriptions in question were of the average type calling for chemicals, galenical preparations, tinctures and fluid extracts. About half of those compounded were materially below the official standards or such standards as were demanded by the physician who wrote the prescriptions. Due allowance was made for deviations in approximate weighing and compounding. The following summary will illustrate the deviations above or below the standards in a number of instances.

Solutions of sodium iodid, 15 to 16 per cent. short and 14 to 21 per cent. in excess. Solutions of potassium iodid, 12 to 70 per cent. short. Solutions of three alkali bromids, 8 to 22 per cent. short. Solutions of strontium bromid, 20 per cent. short to 298 per cent. in excess. Solutions of rubidium iodid, 9 to 36 per cent. short. One party dispensed plain hydrant water in place of the salt.

Guaiaicol.—All samples were below the U. S. Pharmacopoeia standard, varying from —45 to 60 per cent. of true guaiacol.

Iodine Ointment.—Of 14 prescriptions, five were passed as being within reasonable limits. The shortage in iodine varied from 20 to 92 per cent. while that of potassium iodid varied from 14 to 79 per cent. Several specimens were colored brown to cover their deficiency in iodine.

Fluid Extract of Ipecac.—These varied from 24 to 43 per cent. below the standard in alkaloidal content. One sample dispensed was not ipecac.

Fluid Extract of Coca.—While these were fairly good, one party dispensed a fluid not coca extract.

Tincture of Ipecac.—From 16 to 42 per cent. short in alkaloidal content.

Tincture of Opium.—Four samples showed a deficiency, below the standard, varying from —56 to —67 per cent. Another lot, of five, varied from 8 to 15 per cent. below.

Spirits of Camphor.—Two samples out of five were 30 and 37 per cent. short in camphor content.

Solution of Ethyl Nitrite.—The five prescriptions were below the official standard, namely, —10, —25, —37, —44 and —92 per cent. Since manufacturers supply ethyl nitrite in concentrated alcoholic solution, contained in small sealed tubes ready for dilution, there is no excuse for this deficiency. Eight ounces of the sweet spirits of niter were called for.

Fluid Extracts of Pilocarpus.—Belladonna (leaves and root) and Gelsemium were practically all far below normal standards.

Physiological assays of such active drugs as digitalis and strophanthus demonstrated a very wide variation in their relative potency. This demonstrates the necessity of the adoption of physiologic standards.

The retail pharmacist cannot be criticized for the discrepancies occurring among some of the preparations dispensed for he depends upon the wholesaler for his supplies. He should, however, be more discriminating as to the origin of these goods before dispensing for the sick. A careful review of our findings is given

in order to point out the various causes of the deficiencies.

1st. Carelessness in Weighing.—This means careless weighing of the medicinal ingredients that enter either into prescriptions or in making up pharmaceutical preparations. Some pharmacists depend too much on their ability to guess accurately in weighing or measuring, not taking the time to do this as they are taught. There are druggists who measure by eye what they judge to be the accurate volume of a fluid. The majority of samples examined showed gross carelessness in weighing out the medicinal constituents of prescriptions.

2d. Carelessness in Measuring.—This means carelessness in measuring the volume of the fluid in making up prescriptions or pharmaceutical mixtures. We ascribe most of the shortages found to faulty measuring, in that the dispenser simply guessed at the capacity of the bottle used instead of using a graduated measuring vessel. Vials vary considerably in their volume capacity, so then if the dispenser should accurately weigh the medicine and then dissolve it in a fluid without measuring this correctly, naturally the objects of exact dosage will be defeated.

3d. Intentional Short Weighing in compounding prescriptions or making up preparations where expensive ingredients are to be used. For example, potassium iodide, 8.9 grams, instead of 30 grams as ordered in solution. Rubidium iodide, 0.96 gram, in place of 1.5 grams in solution. Ammonium iodide, 3.8 grams, instead of 5 grams. Tinctures of opium, 0.4 and 0.5 gram morphine in 100 cc., instead of 1.2 to 1.25 grams as the Pharmacopoeia demands. Ointments of iodine containing 25 to 40 per cent. less iodine than the standards demand, etc., etc.

4th. Deliberate Fraud.—Cases of this kind are rare among pharmacists, and when they occur, should be severely punished. Such practices are not countenanced anywhere. For example, the dispensing of water for a valuable medicinal agent as rubidium iodide; the substitution of an inert preparation instead of an active one, as in the case of fluid extract of coca or ipecac; the sale of tablets adulterated with a foreign chemical instead of the one prescribed; the use of colored lard in making up iodine ointment in order to cover the deficiency in iodine.

5th. Addition of Foreign Chemicals to Improve Appearances.—There is no excuse for adding "hypo" to solutions of potassium iodide when prescribed by a physician, nor any other preservative without his knowledge. Solutions of this chemical keep very well. Also inexcusable is the substitution of petrolatum (vaseline) in place of benzoinated lard in pharmacopoeial preparations where this ointment vehicle is specifically ordered. There are definite medical grounds for using the one (lard) or the other (petrolatum). If changes are made by the dispenser, the physician should be so informed.

6th. Market Supply.—Practically all of the drugs and chemicals obtained through reputable wholesalers are fully up to the rigid requirements of the U. S. Pharmacopoeia. Unfortunately, however, there

are many unscrupulous dealers and peddlers of low-grade and rejected drugs, who impose on easy-going although well-meaning, druggists struggling for an existence. Let it be distinctly understood that at no time does a pharmacist experience any difficulty in obtaining drugs of the highest quality. It is only when seeking cheap stuff that he is imposed upon.

7th. Deterioration.—Some chemicals undergo rapid deterioration in spite of all efforts to the contrary. In such cases the manufacturer provides means of supplying the article in small packages or partially prepared so that the prescription may be made of fresh new material. We refer more particularly to sweet spirit of niter. This will not keep its strength up to the standards set for any length of time, hence, must be made fresh when called for. Since our manufacturers provide especially for the quick dispensing of full strength spirit of niter, there can be no excuse for dispensing preparations containing only 0.3, 2.2 and 2.5 per cent. when the standard requires that at least 4 per cent. should be present.

8th. Adulteration.—This represents one of the worst phases of the evil, since the motives are purely for gain, while deception and fraud are perpetrated upon the sick and injured, a crime of the worst type. *This practice is confined to circles outside of our dispensing druggists.* It occurs among the crude and powdered botanic drugs and more especially in the important medicinal organic chemicals which are extensively used in modern medicine. Many of the more popular of this class of remedies are peddled about by wandering dealers and firms of many aliases, who, when necessary, cross the border, or are now located there. These men do a prosperous business in selling these imitations and "just-as-good" products.

9th. Substitution.—This practice consists in substituting a drug of similar therapeutic action in place of one prescribed, either because it may be cheaper or because the pharmacist may be out of the desired article, or through carelessness. Several instances of this kind occurred: some were the substitution of an entirely different drug for that prescribed by the physician. Other cases were of a harmless nature, but still open to censure on grounds of carelessness. We refer to the substitution of the fluid extract of the "leaf" for that of the "root." There is a difference in the degree of activity (therapeutic) of the preparations of the leaves and roots of various drugs as well as a decided difference in color.

The New York College of Pharmacy, as well as other colleges of pharmacy and their graduates, who make up a very large proportion of our best dispensing pharmacists, maintain the highest standards of service and use every endeavor to protect the practice of pharmacy along correct and scientific lines. Our first national law regulating the importation of drugs and chemicals, enacted in June, 1848, was the result of action taken by the New York College of Pharmacy, seconded by medical and other pharmaceutical colleges.

This action also resulted in the organization of the American Pharmaceutical Association, whose

aims have been solely to promote the practice of pharmacy along scientific and ethical lines. This war on substitution and sophistication of medicines has been constantly waged with varying results, chiefly owing to faulty legislative action or difficulties in enforcing the laws already enacted. As the matter now stands, the market is abundantly sup-

plied with the purest of drugs and chemicals supplied by manufacturing firms whose names are guarantees for the very best that skill and science can produce. If our druggists will buy only from such houses and employ competent, conscientious assistants, they will render such service as the public has a right to expect.

VIRGIL COBLENTZ.

ORIGINAL PAPERS.

THE ELECTRICAL PRECIPITATION OF SUSPENDED PARTICLES.

By F. G. COTTELL.

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The removal of suspended particles, from gases, by the aid of electric discharges is by no means a new idea. As early as 1824 we find it suggested by Hohlfeld¹ as a means of suppressing ordinary smoke, and again a quarter of a century later by Guitard.² These suggestions, which do not seem to have stimulated any practical study of the question, were soon entirely forgotten and only brought to light again by Sir Oliver Lodge³ many years after he himself had independently rediscovered the same phenomena and brought them to public attention⁴ in a lecture before the Liverpool Section of the Society of Chemical Industry Nov. 3, 1886. The first recorded attempt to apply these principles commercially appears to have been made at the Dee Bank Lead Works. The general principle of electrical precipitation of suspended matter was at this time patented by Alfred O. Walker of the above firm in several countries,⁵ but these patents have long since expired. The apparatus was installed in 1885 by the works manager, W. M. Hutchings, with the coöperation of Prof. Lodge and briefly described by the former⁶ just before its completion as consisting of a system of metallic points situated in the flue from the lead furnaces and excited from two Wimshurst influence machines with glass plates 5 ft. in diameter, each machine being driven by a one-horse power steam engine.

The apparatus undoubtedly did not in practice fulfil expectations as we find nothing further of it in the literature. The most apparent weakness of the project lay perhaps in the reliance on the Wimshurst machine, which had then just been brought out and from which a great deal more was anticipated⁷ than has been justified by experience, at least as far as commercial applications are concerned.

Since that time an occasional patent¹ or article² has served to keep the subject in the public eye and in 1903 Lodge himself took out a patent³ covering the use of the then new mercury arc for rectifying high potential alternating currents for this purpose.

Up to the present time none of these patents seem to have been carried into successful commercial operation on the large scale in the chemical or metallurgical industries.

Some four years ago while studying various methods for the removal of acid mists in the contact sulfuric acid process, the author had occasion to repeat the early experiments of Lodge and became convinced of the possibility of developing them into commercial realities. The work described in the present paper may fairly be considered as simply the reduction to engineering practice as regards equipment and construction of the fundamental processes long since laid open to us by the splendid pioneer work of Lodge, a feat vastly easier to-day than at the time of Lodge and Walker's original attempt.

The precipitation of suspended matter whether in gases or liquids may be accelerated by electricity in the form of either direct or alternating current, but the mode of action and the type of problem to which each is best applicable differ in certain important respects.

Where an alternating electromotive force is applied to a suspension the action consists for the most part in an agglomeration of the suspended particles into larger aggregates out in the body of the suspending medium and a consequently more rapid settling of these aggregates under the influence of gravity.

Thus if powerful Hertzian waves are sent out into foggy air the alternating fields set up in space cause an agglomeration of the particles of liquid into larger drops which then settle much more rapidly. Considerable work aimed at the application of this phenomena to the dispelling of fog on land and sea has recently been done in France and England but very little as to definite results seems as yet to have been published. The field appears, however, one of considerable promise. Another application of alternating current along these lines is found in a process now in use in the California oil fields for separating emulsified water from crude oil. This process grew out of the work here described and was developed some

¹ "Das Niederschlagen des Ranchs durch Electricität Hohlfeld," *Kastner Archiv. Naturl.*, **2**, 205-6 (1824).

² C. F. Guitard, *Mechanics Magazine*, Nov., 1850.

³ Historical Note on "Dust Electrification and Heat," O. J. Lodge, *Nature*, **71**, 582 (1905).

⁴ "The Electrical Deposition of Dust and Smoke with Special Reference to the Collection of Metallic Fumes and to a Possible Purification of the Atmosphere," *J. Soc. Chem. Ind.*, **5**, 572-6 (1886), with appended bibliography.

⁵ Great Britain, 11,120, Aug. 9, 1884; Belgium, 68,927, May 19, 1885; Spain, 7,211, July 10, 1885; Germany, 32,861, Feb. 27, 1885; Italy, 18,007, Mar. 31, 1885; United States, 342,548, May 25, 1886.

⁶ *Berg- und Hüttenmännisch. Zeitung*, **44**, 253-4 (1885).

⁷ A. O. Walker, *Engineering* (Lond.), **39**, 627-8 (1885). G. Tissandier, *London Electrician*, **17**, 33 (1886).

¹ Lorrain, British Pats., 6495 and 6567 (1886); Thwait, U. S. Pat., 617,618, Jan. 10 (1899); Hardie, U. S. Pat., 768,450, Aug. 23 (1904).

² J. Wright, *Elect. Rev.* (Lond.), **47**, 811, Nov. 23 (1900), see also *Jour. Roy. Sanitary Institute*, **27**, 42.

³ Brit. Pat., 24,305 (1903); U. S. Pat., 803,180, Oct. 31 (1905).

two years ago by Mr. Buckner Speed and the author to meet certain peculiar conditions existing in these fields, but as it is to be described more at length in a subsequent article the details will be here omitted.¹

Alternating current may thus be used to advantage where the masses of gas or liquid to be treated are fairly quiescent and a simple agglomeration of the suspended particles into larger aggregates is sufficient to effect separation by gravity or otherwise.

In the case of the large volumes of rapidly moving gases in smelter flues the agglomerating and settling process is, however, too slow even when the flues are expanded into as large dust chambers as are commercially feasible. It is in such cases that direct current methods have been particularly important.

If we bring a needle point connected to one side of a high potential direct current line opposite to a flat plate connected to the other side of the line we find that the air space between becomes highly charged with electricity of the same sign as the needle point irrespective of whether this is positive or negative, and any insulated body brought into this space instantly receives a charge of the same sign. If this body is free to move, as in the case of a floating particle, it will be attracted to the plate of opposite charge and will move at a rate proportional to its charge and the potential gradient between the point and plate.

Even if there are no visible suspended particles the gas molecules themselves undergo this same process, as is evidenced by a strong wind from the point to the plate even in perfectly transparent gases. The old familiar experiment of blowing out a candle flame by presenting it to such a charged point is simply another illustration of the same phenomena.

As above indicated the first step toward practicality was of necessity a commercially feasible source of high tension direct current. The obstacles to building ordinary direct current generators for high voltages lie chiefly in difficulties of insulation, and if this is avoided as to individual machines by working a large number in series the multiplication of adjustments and moving parts intrudes itself. On the other hand, high potential alternating current technique has in late years been worked out most thoroughly, and commercial apparatus up to 100,000 volts is available in the market. The mercury arc rectifier has been made practical for series arc lighting service up to some 5000 volts direct current, but although higher voltage units were at one time attempted by the electrical companies they were later withdrawn from the market as unsuited to practical operating conditions. For high voltages they seem like the static machines to work well under the careful management and light duty of the laboratory but to fail in practice. This is particularly so in the application to metallurgical and chemical work where the electrodes in the flues have to be placed close together and worked near the potential of disruptive discharge, the occasional occurrence of which later places much more severe requirements upon generating apparatus

than in the case of the series arc lighting, to which the rectifier seems particularly well adopted.

This restriction does not necessarily apply to the conditions under which fog and smoke would be treated in the open air. It is to these latter cases that Lodge's efforts in late years seem to have been the more particularly directed, and here the mercury rectifier in connection with high potential transformers may find a useful field.

The procedure actually used in the installations described below consists in transforming the alternating current from an ordinary lighting or power circuit up to some 20,000 or 30,000 volts and then commutating this high potential current into an intermittent direct current by means of a special rotary contact maker driven by a synchronous motor. This direct current is applied to a system of electrodes in the flue carrying the gases to be treated.

The electrodes are of two types corresponding to the plate and point in the experiment above cited. The construction of electrodes corresponding to the plate presents no special problem as any smooth conducting surface will answer the purpose. With the pointed or discharge electrodes it is quite otherwise and the working out of practical forms for these has proved the key to much of the success thus far obtained.

In laboratory experiments when the discharge from a single point or a few such is being studied fine sewing needles or even wire bristles answer very well, but when it is attempted to greatly multiply such discharge points in order to uniformly treat a large mass of rapidly moving gas at moderate temperatures great difficulty is met in obtaining a powerful and, at the same time, effective distribution of current.

It may be of interest to note that the clue to the solution of this difficulty came from an almost accidental observation. Working one evening in the twilight when the efficiency of the different points could be roughly judged by the pale luminous discharge from them, it was noticed that under the particular conditions employed at the time, this glow only became appreciable when the points had approached the plates almost to within the distance for disruptive discharge, while at the same time a piece of cotton-covered magnet wire which carried the current from the transformer and commutator to the discharge electrodes, although widely separated from any conductor of opposite polarity, showed a beautiful uniform purple glow along its whole length. The explanation lay in the fact that every loose fiber of the cotton insulation, although a relatively poor conductor compared to a metallic point, was still sufficiently conductive from its natural hygroscopic moisture to act as a discharge point for this high potential current and its fineness and sharpness, of course, far exceeded that of the sharpest needle or thinnest metallic wire. Acting on this suggestion it was found that a piece of this cotton-covered wire when used as a discharge electrode at ordinary temperature proved far more effective in precipitating the sulphuric acid mists, which were then the object of study, than any system of metallic

¹ See also "Dehydration of Crude Petroleum, a New Electrical Process," Arthur T. Beazley. *The Oil Age*, 3, 2-4, Apr. 21, 1911.

points which it had been possible to construct. Perhaps the greatest advantage thus gained lay in the less accurate spacing demanded between the electrodes of opposite polarity in order to secure a reasonably uniform discharge.

In practice of course a more durable material than cotton was demanded for the hot acid gases to be treated and this has been found in asbestos or mica, the fine filaments of the one and the scales of the other supplying the discharge points or edges of the excessive fineness required. These materials are twisted up with wires or otherwise fastened to suitable metallic supports to form the discharge electrodes in such wise that the current has to pass only a short distance by surface leakage over them, the slight deposit of moisture or acid fume naturally settling on them serving to effect the conduction. If the condition of the gases does not supply sufficiently such coating then a special treatment of the material before being placed in the flue is resorted to.

The construction and arrangement of the electrodes as also of the chamber containing them naturally varies very widely with the conditions to be fulfilled under the varied applications to which the process may be put. Some of the more general features of this work are described in the patents¹ already issued in this and foreign countries, while further details and modifications are covered in other patents not yet issued from the Patent Office. The accompanying photographs give perhaps a better idea of the gradual development of the work than any detailed description which would be possible in the space here at command.

Fig. 1 is the apparatus used for the original laboratory experiments in the spring of 1906. Sulphuric acid mist was generated by bubbling the gas from the little contact sulphuric acid plant, seen on the table, through water in the U-tube beneath the inverted glass bell jar, whose inner walls were quickly wetted sufficiently with acid to act as the collecting electrode, a wire being inserted along side of the stopper through which the U-tube connected with the bell jar and served to connect the jar walls to the induction coil on the left, the latter acting as the step-up transformer. This coil received alternating current at 110 v. from the lighting circuit and gave about 3700 volts at its secondary. The other high potential terminal of the induction coil was connected to the discharge electrode within the bell jar through a make and break operated by the synchronous motor. This latter was improvised by substituting a plain iron cross for the squirrel cage armature in an ordinary fan motor operated from the same 110 v. line as the induction coil, and brought into step by the induction motor on the right. A momentary contact with the discharge electrode was thus established once each complete cycle at the peak of the voltage wave, and served to charge this electrode to the maximum voltage of the line, always with the same polarity. In order to help maintain the charge on the electrode in the interval between

these contacts the Leyden jar seen in the picture was connected in parallel with the electrodes. The wire leading to the jar walls or collecting electrode was usually grounded for convenience and safety, as in fact has been done throughout all the practical installations. This leaves but one high potential conductor to deal with in each precipitation chamber and greatly increases the safety of operation.

Fig. 2 is a closer view of the precipitation chamber through which the acid fume is being blown at the rate of about 20 liters per minute, the electric current being shut off of the apparatus. Fig. 3 shows the effect of turning on the electric current with the same gas steam still flowing.

The discharge electrode in this case consisted of a cylinder of wire screen wrapped with a few turns of asbestos sewing twine and suspended by a wire passing through a glass tube as shown. The suspended particles of acid were driven away from the asbestos filaments and deposited on the walls of the bell jar, finally running down into the U-tube below.

The next undertaking was to duplicate these experiments on a scale some two-hundred-fold larger. This was carried out during the same summer at the Hercules Works of the E. I. du Pont de Nemours Powder Company at Pinole on San Francisco Bay, where the contact gases from one of their Mannheim contact sulphuric acid units were kindly placed at our disposal. These gases at the point selected contained about 4 per cent. by volume of dry gaseous sulphur trioxide, and in order to convert this into sulphuric acid mist they were brought in contact with water. Under these conditions very little of the sulphur trioxide is absorbed by the liquid water, but the latter evaporating into the gas combines with the sulphur trioxide to form the far less volatile sulphuric acid which immediately separates as a dense white cloud of suspended particles so fine as to represent one of the most difficult of all materials to remove by filtration.

Figs. 4 and 5 are photographs taken about a minute apart with the same current of fume-laden gases passing into the precipitation chamber, but with the electric current respectively off and on. The apparatus was the same in general plan as the small laboratory unit described above, except that instead of a single cylinder of wire screen for the discharge electrode, two concentric cylinders were used, while intermediate in diameter between these two and resting on the lead pan bottom of the apparatus was a third cylinder, also of iron wire screen, but without asbestos winding, which together with the outer leaded glass cylinder constituted the collecting electrodes. The precipitated acid drained off from this precipitation chamber into the carboy on the right. The space between successive cylinders of opposite polarity was as nearly as possible an inch and a quarter. Current was supplied from three 1-kw. 110 v. to 2,200 v. transformers connected in series on their 2200 v. side to give 6600 v. The fume was delivered as before to the bottom of the precipitation chamber at its center and had to pass through the three-wire cylinders and

¹ U. S. Pats., 866,843, 895,729 and 945,717. The second of these also practically reprinted by *Eng. Min. J.*, 86, 375-7 (1908).

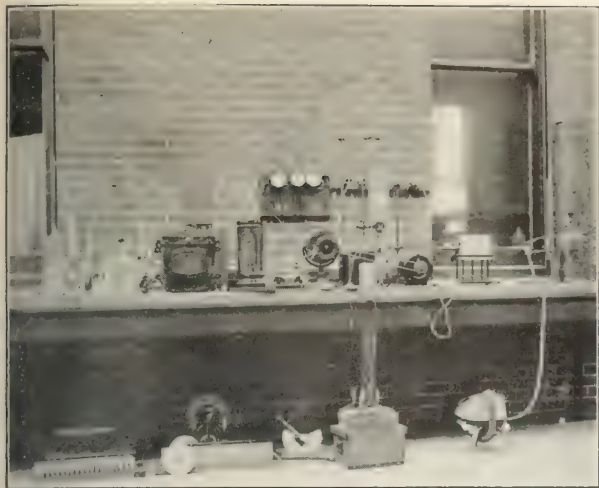


Fig. 1.



Fig. 2.

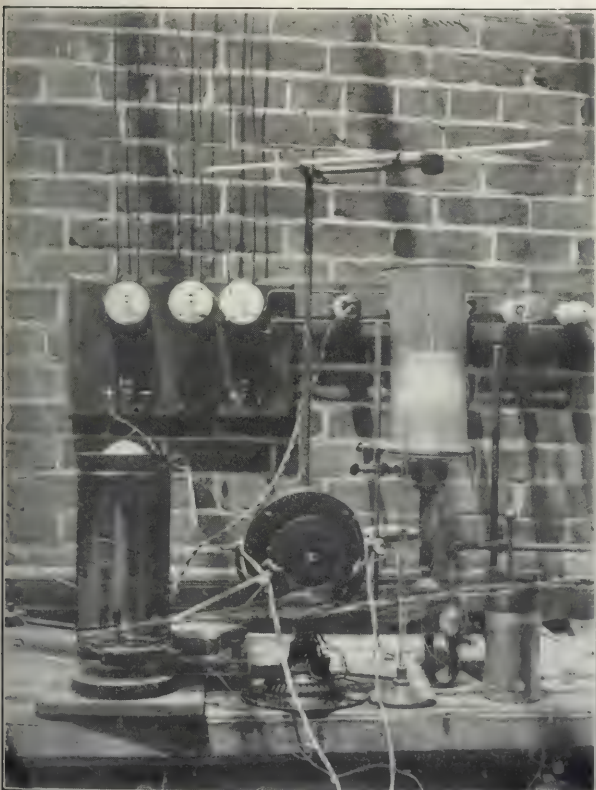


Fig. 3.

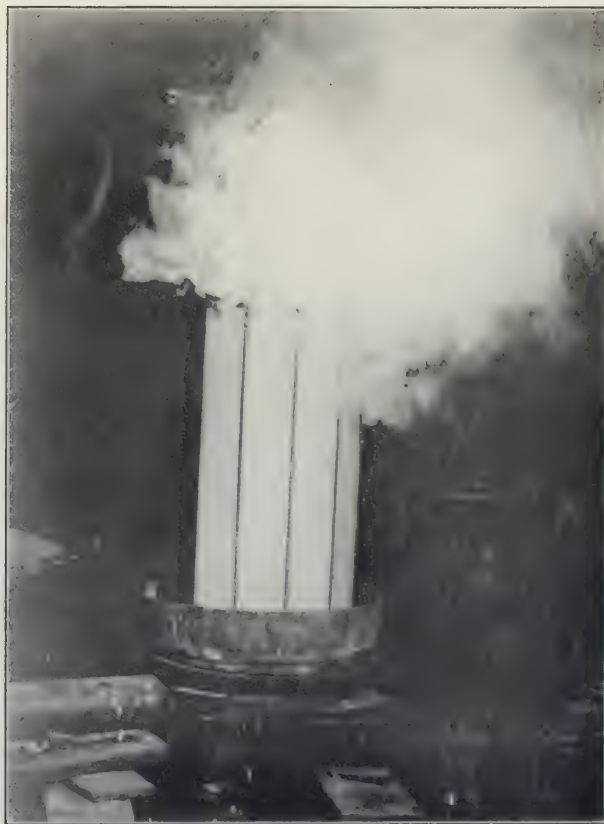


Fig. 4.

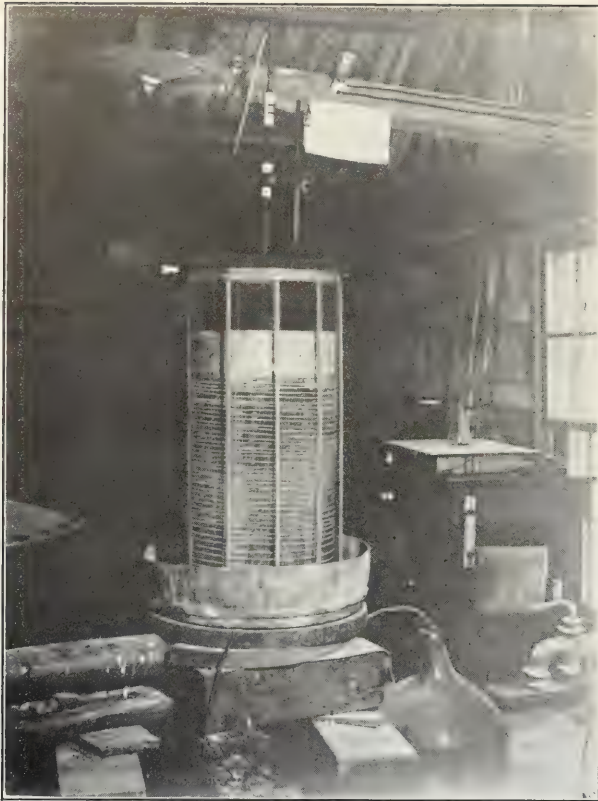


Fig. 5.



Fig. 6.

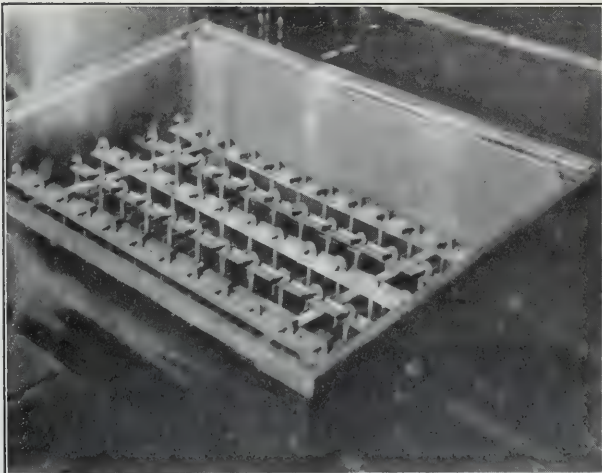


Fig. 7.



Fig. 8.



Fig. 9.



Fig. 10.

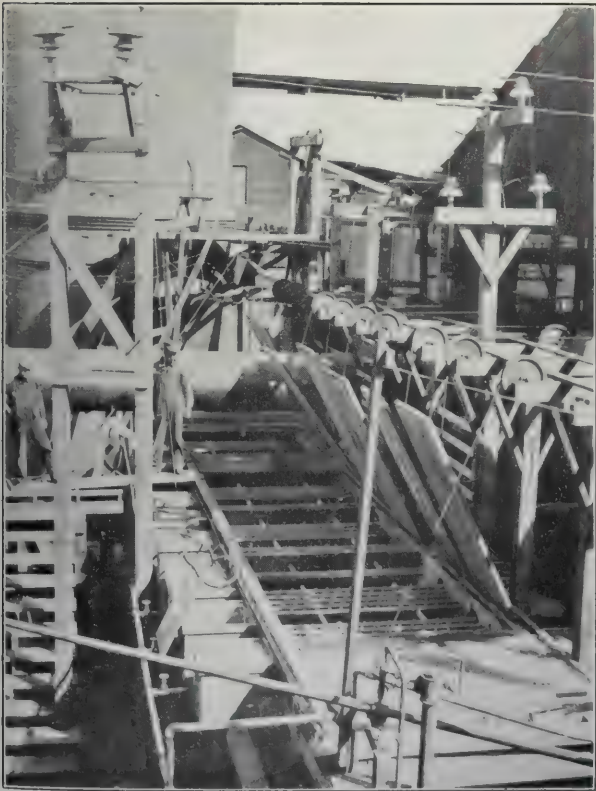


Fig. 12.

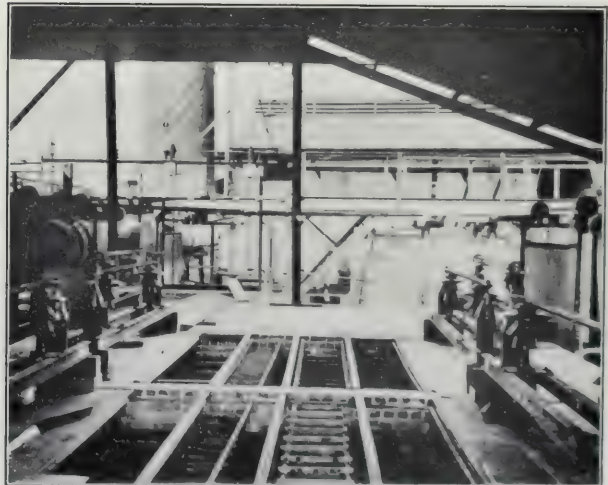


Fig. 11.



Fig. 13.



Fig. 14.



Fig. 15.



Fig. 16.

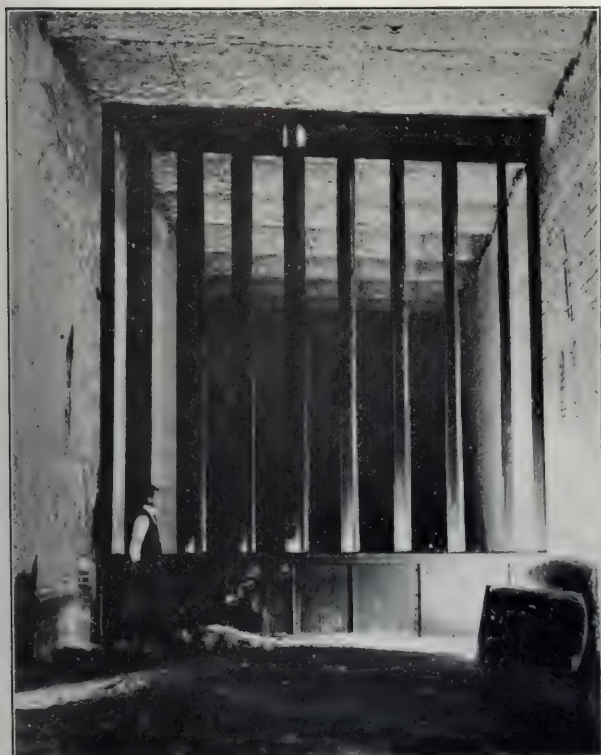


Fig. 17.



Fig. 18.



Fig. 19.



Fig. 20.

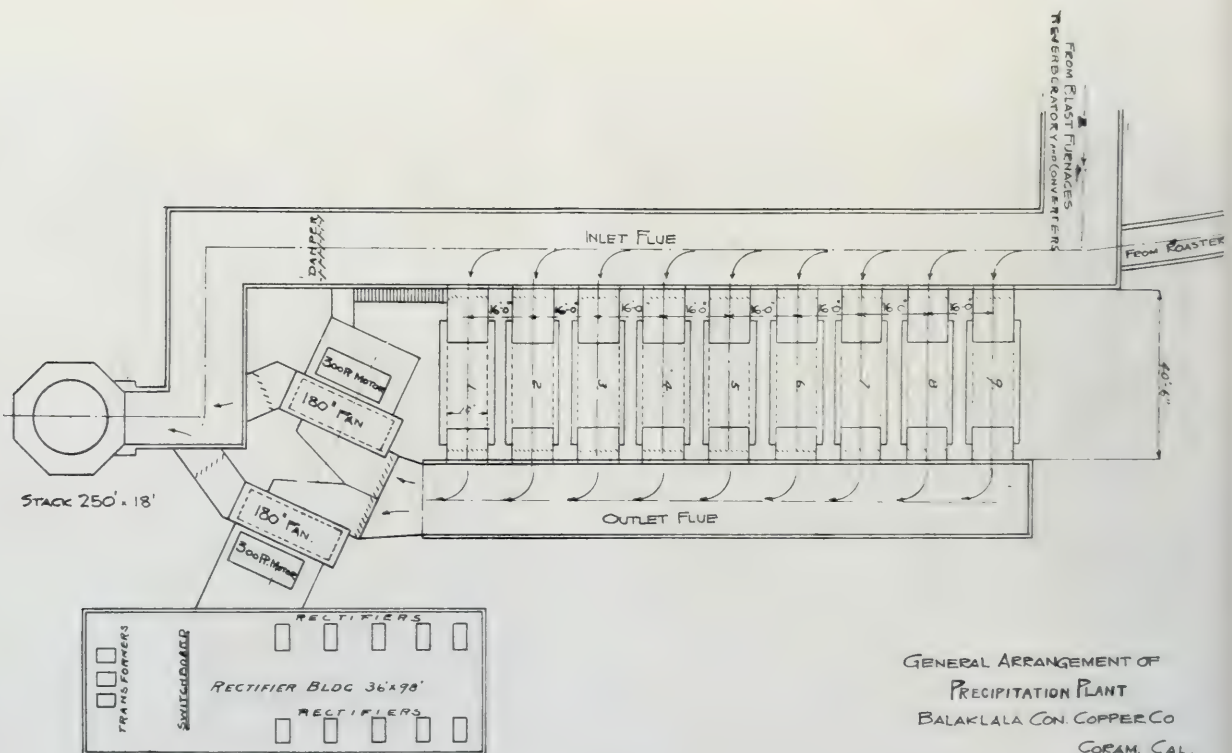


Fig. 21.

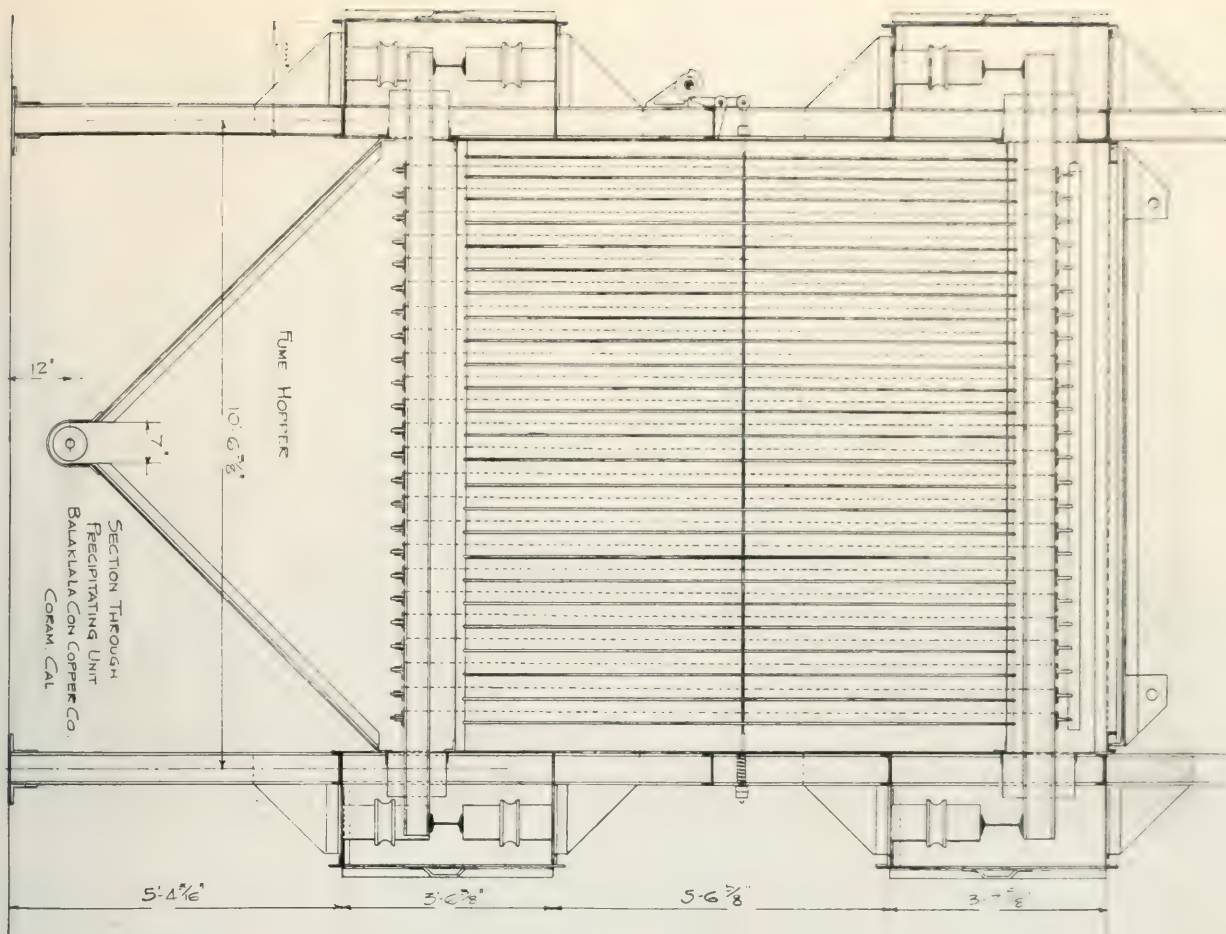


Fig. 22.

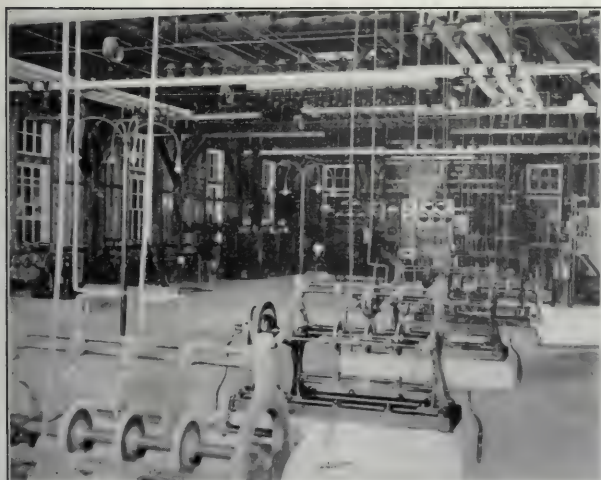


Fig. 23.



Fig. 24.

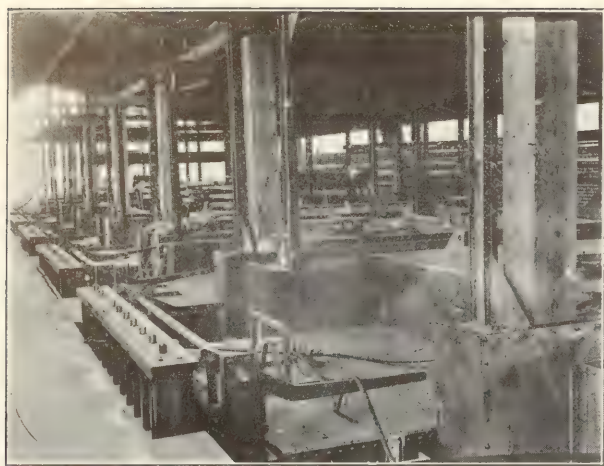


Fig. 25.



Fig. 26.



Fig. 27.



Fig. 29.

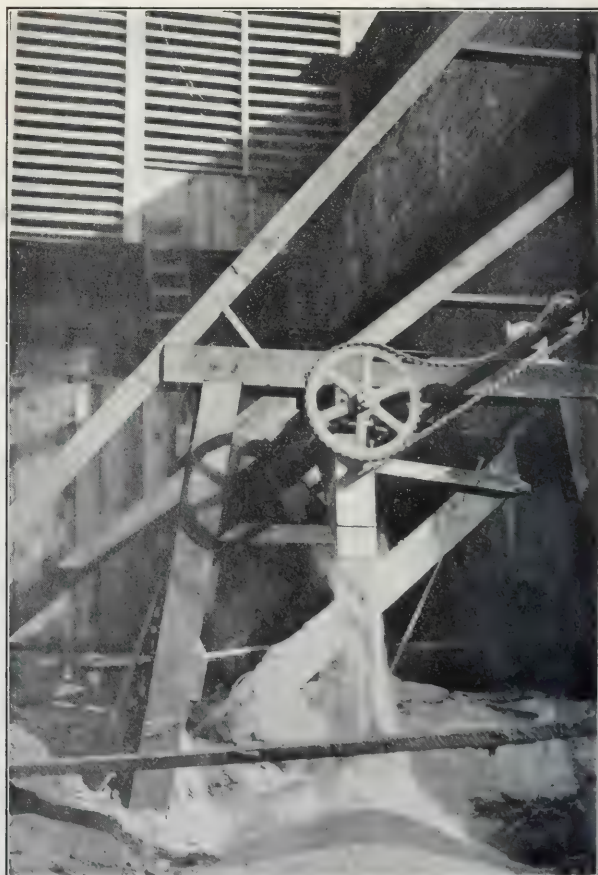


Fig. 28.

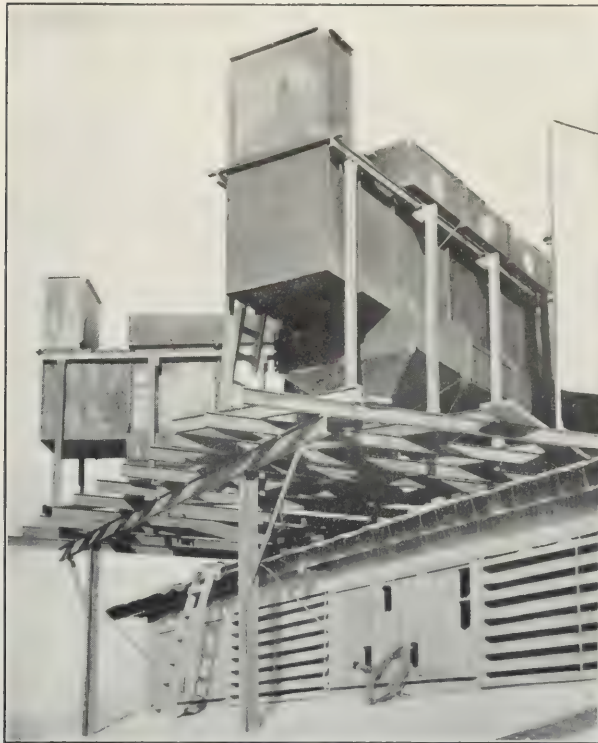


Fig. 30.

up between the outer of these and the glass container, thus being subjected to three electric fields in succession. In this apparatus the power consumption was about one-fifth of a kilowatt, and between one hundred and two hundred cubic feet of gas per minute could readily be treated. This apparatus was of course merely for experimental and demonstration purposes but a still larger unit built for permanent operation and to handle all of the gas from a Mannheim unit has since been installed at this plant and put into steady commercial operation.

These experiments at Pinole attracted the attention of the Selby Smelting and Lead Company whose smelter located at Vallejo Junction a few miles farther up the Bay was at that time the object of injunction proceedings brought by the farmers of the surrounding country. At the time the suits originated three separate stacks at the Smelter contributed to the alleged nuisance. The first, and admittedly the most serious offender, handled the gases from the lead blast furnaces and discharged several tons of lead fume daily into the air. Shortly before the commencement of our work at the plant this had been obviated by the installation of the bag house¹ shown in Fig. 6. After correcting this evil there still remained, however, a stack discharging the gases from the roasters, which besides the invisible sulphur dioxide furnished dense white clouds consisting chiefly of sulphuric acid, arsenic and lead salts, and to which the bag house was inapplicable on account of the corrosive action of these gases upon the bags. Lastly there was the stack of the refinery carrying the mists escaping from the pots of boiling sulphuric acid used to dissolve the silver out of the gold and silver alloy coming from the cupels.

The blast furnace and the roaster stacks each carried something over 50,000 cu. ft. of gas per minute while the refinery stack represented scarcely a tenth of this volume. As a first step we accordingly commenced operations on this latter, and after several months' experimenting, as to the best form of construction, adopted a system of vertical lead plates 4 in. wide by 4 feet in length and spaced about 4 in. apart. Several rows of such plates were assembled in a 4 by 4 foot lead flue. Between each pair of plates hung a lead-covered iron rod carrying the asbestos or mica discharge material, the latter finally proving the more serviceable in this highly acid atmosphere. These rods or discharge electrodes were supported on a gridwork of buss bars extending over the heads of the plates and through apertures in the sides of the flue to insulators on the outside. Fig. 7 is a view looking down on the top of this flue with the cover removed from above the electrodes. Figs. 8 and 9 show the effect on the appearance of the stack when the electric circuit is respectively open and closed, the stack in the immediate left foreground being the one into which this flue discharges. The large stack in the middle background is from the roasters to be discussed below. Fig. 10 shows the corresponding stream of dilute sulphuric acid (about

40° Bé.) running out from the flue as precipitated. When the acid kettles are at a full boil it often amounts to over two gallons a minute.

The electric current is taken from the power circuit of the plant at 460 volts, 60 cycles, and transformed up to 17,000 volts thence through the synchronous contact maker or rectifier to the electrode system. At first a glass plate condenser was connected across the high potential line in parallel with the electrode system in order to assist in maintaining the potential of the electrodes between the intervals of contact but was found troublesome and unnecessary in practice and in this and other installations is now omitted.

The power consumption for this installation is about 2 kw. including the driving current for the synchronous motor. The switchboard transformer and rectifier are located in the engine room of the plant and require no more attention than a feed pump or a blower. The installation has now been in successful daily operation for over three years at a cost for labor attendance and repairs of less than \$20 a month. In fact while the plant was making enough bluestone to utilize all the weak acid recovered, the saving on purchase of the latter paid for the entire cost of operating five times over.

The next undertaking was naturally an extension of the process to the treatment of the gases coming from the pyrites and matte roasters of the same plant. This presented a somewhat more difficult problem as the material to be removed consisted of a mixture of solid dust and fume with liquid sulphuric acid. From small scale experiments it was at first thought possible to precipitate the material in a reasonably dry form and shake it in this condition from the electrodes, thus permitting of brick and iron construction. Quite an extensive installation was carried through on this plan, a general view of which is seen in Fig. 11. It consisted of four parallel brick flues or chambers each 22 ft. long, 7 feet wide and 9 feet deep, and containing an electrode system of iron plates as grounded or collecting electrodes and wire and asbestos discharge electrodes somewhat similar in general arrangement to that in the refinery flue. In this case, however, the insulating supports of the discharge electrodes were carried above the flue as seen to right and left in the figure.

In practice, however, this type of equipment was found poorly adapted to the particular gas conditions here met with, as a very much higher proportion of free sulphuric acid was encountered than the preliminary tests had given reason to expect, the weight of this free acid often exceeding, in fact, that of all the solids in the gas put together. The gases were also highly charged with water vapor both from the wet ore and the steam atomizing oil burners in the roasters, and this tended further to dilute the acid and produce a muddy deposit. The iron and brick construction made removal of this deposit by washing impracticable so it was decided to further cool the gases and treat them in a lead flue similar to that used in the case of the refinery. However, the experience gained with the large brick flues in which a wide

¹ For detailed description see *Eng. Min. J.*, 86, 451-7 (1908).

variety of electrodes were tested out, made it possible to compress this new construction into far smaller compass than would otherwise have been thought possible.

The resulting construction is seen in Fig. 12. This is a sheet lead flue 6×6 feet cross section and 32 feet long, containing 38 rows of 16 lead plates each 6 feet long by 4 in. wide with the corresponding discharge electrodes between each pair. The effect of the treatment upon the appearance of the gases issuing from the stack is shown in Figs. 13 and 14 which, as before, represent respectively the electric current switched off and on being taken about three minutes apart. When Figs. 6 and 12 are compared and it is remembered that in this 32 feet of 6×6 ft. flue about the same volume of gases was being treated as in the bag house measuring about $98 \times 125 \times 55$ feet, and further that actual tests showed that even the woolen bags used in this bag house are completely destroyed by these roaster gases in less than half an hour, a better idea may be gained of some of the possibilities which this process appears to open. The power consumption in this case was between 10 and 15 kw. The material precipitated upon the plates was a grayish mud easily washed off and drained out through the bottom of the flue to settlers. For this purpose it was necessary once in about every four to six hours to by-pass the gases, shut off the current from the flue, raise its covers as seen in Fig. 12 and close down the electrodes from above. One man could easily carry out this whole operation in from five to ten minutes. For continuous operation on such material it is, of course, necessary to subdivide the treatment into two or more units in order that while one is being cleaned the others may be in operation.

In order to insure that essentially all the free sulphuric acid and arsenic of these roaster gases should be condensed from true gases into suspended particles, which latter are all the apparatus purports to collect, and also to protect the lead construction from softening from the heat, it was found necessary to cool the gases down to less than 150°C . To accomplish this a system of water sprays was first used in the mouth of the lead flue just before the electrodes. This served the purpose very well as long as clean water which would not stop the sprays was available, and successful test runs of a week or more duration were made with this system, but as the circulating and cooling water of the entire plant is derived from the Sacramento River, which is often very muddy, the difficulties of keeping the sprays clean and open determined the management of the plant to resort to cooling by radiation through a lengthening of the flue before the precipitator. This construction and the refitting of the apparatus for continuous operation has not as yet been undertaken, and as the litigation with the farmers seems for the present at least to have centered more about the question of sulphur dioxide, it is likely that the completion of the work will be allowed to await the reaching of an understanding on this matter.

The next installation in order of size to be undertaken was at the Balaklala Smelter at Coram, Shasta County, California. The vast body of low-grade copper ore reaching for many miles across this county and commonly known as the Copper Crescent has recently been described in detail by L. C. Grafton¹ and characterized as the second largest copper deposit which can be considered as a single geological unit in the United States.

The first commercially successful smelter in this region was erected at Keswick in 1896 by the Mountain Copper Co., Ltd., under the management of Louis T. Wright and was of especial interest as one of the pioneers in pyritic smelting. Extensive heap roasting was also carried on at this plant with the result of wide-spread deforestation of the surrounding country and the final closing down of the plant in 1905 through injunction proceedings instituted by the U. S. Forestry Service. The company has since built a small smelter and acid phosphate works at Martinez on San Francisco Bay and now ships its ore to this point nearly 250 miles distant for treatment, but even this latter plant has at various times come in for its share of fume litigation.

In 1901 the Bully Hill Smelter at Delamar with a capacity of 250 tons a day was started. This was later purchased and is now owned by the General Electric Company, but since last July it has been closed as a result of complaints by the U. S. Forestry Service who insisted, at that time, that the plant either close or at least commence efforts on a practical scale looking toward controlling its fumes.

In 1905 the Mammoth Copper Mining Company, a subsidiary of the U. S. Smelting, Refining and Mining Company, blew in its present smelter at Kennett. This plant when running full has a capacity of some 1200 tons of ore per day.

The Balaklala, or First National Copper Company, is the most recent of the Shasta County smelters, having blown in its first furnace in 1908.

These smelters are all situated in the narrow precipitous cañon of the upper Sacramento River and its tributary, the Pitt. The region itself is too steep and rocky for agriculture but was once heavily wooded, although now swept bare of vegetation for miles. As far as the cañon itself is concerned probably all the damage possible has already been done unless reforestation were undertaken. This latter even would probably be slow and difficult work as since the loss of vegetation the steep hillsides have been washed bare of soil for miles around. At Redding, however, some 13 miles below Coram and 17 miles below Kennett, the cañon widens out into the fertile Sacramento valley and from this point southward for some 12 miles further lies the region from which for the past two years have come increasingly insistent complaints against the smelters. These culminated a little over a year ago in agreements between the farmers and the smelters under which friendly suits were brought in the federal courts and injunctions issued by stipulation requiring the smelters to remove the suspended matter from their exit gases and dilute

¹ U. S. Geological Survey, *Bull.* 430b.

the latter to such an extent that their sulphur dioxide content should not exceed seventy-five hundredths of one per cent. by volume as discharged from the stacks, with the further general and sweeping provision that they should do no damage.

To accomplish this the Mammoth Smelter installed a bag house which has been in very successful operation since last July. Fig. 15 is a view of this plant showing the bag house on the left in operation. It will be noted that the gases discharged from the five stacks (each 21 feet square) are to all intents and purposes free from suspended matter and consequently invisible. This represents a notable achievement, being the first time that the bag house, so efficient in lead smelters, has been successfully applied to copper blast furnace gases on the large scale.

It is made possible in this instance through neutralization of the sulphuric acid in the gases by the zinc oxide carried over in the fume from the very heavy zinc content of the ore smelted. The Company is also the owner of patents¹ on the introduction of finely divided metallic oxides into the gases for this purpose. In addition it was necessary to provide an extensive system of cooling pipes seen in front of the bag house in the picture. There are 39 of these pipes each 4 feet in diameter and averaging about 200 feet in length. They represent a very large part of the cost of the installation. It was expected that they would be sufficient to cool the entire gases of the plant to a safe temperature to protect the \$30,000 worth of woolen bags with which the house is filled, but upon starting up it was found that only a little over half the full capacity of the plant could thus be treated with safety and operations were accordingly restricted to this. In the cold weather of winter a considerably larger tonnage can be handled with safety than during the hot summer. Notwithstanding this, however, the bag house is to be considered a decided success at least for the particular conditions met with at this plant and the management deserves great credit for the courage and skill with which it has carried through this new, and after all largely experimental, undertaking, representing as it does the expenditure of over a quarter of a million dollars.

In the case of the Balaklala Smelter, of which Fig. 16 is a general view, the use of a bag house was also considered and in fact a small experimental unit containing a few bags was run for some months in comparison with tests both by the electrical process here described and also a centrifugal apparatus in which the gases passed through a rapidly rotating cylindrical shell equipped with radial baffles to insure the gas being raised to full velocity. As a result of these tests the electrical process was adopted for the full-sized installation.

The smelter treats from 700 to 1000 tons of $2\frac{1}{2}$ to 3 per cent. ore carrying over 30 per cent. of sulphur with considerable but varying amounts of zinc. The greater proportion of this is handled in blast furnaces but the fines including everything under an inch and

amounting to less than 10 per cent. of the whole go through MacDougal roasters and an oil-fired reverberatory. The plant has also two converter stands. The gases from all these departments pass into a common flue 18 × 20 feet in cross section, an interior view of which at the main by-pass damper is shown in Fig. 17. The volume of gases passing through this flue varies with operating conditions from a quarter to half a million cubic feet a minute which means in round numbers a mean linear velocity in the flue shown of 10 to 20 feet per second.

Before attempting to design the full-sized equipment for treating these gases a small precipitation chamber capable of treating about 1 per cent. of the total gases was erected and an extended set of experiments made with it. Fig. 18 shows this small unit with its exhaust fan and stack. In the original tests it was located nearer the base of the main stack, the figure showing it in its present state as modified for other experiments and tests.

Figs. 19 and 20 indicate the degree of success attained with this small unit in its original position having been taken a few minutes apart with the electric current respectively off and on, the same gas volume issuing in both instances from the stack which is 2 ft. in diameter.

With this miniature unit as a guide the equipment of the whole plant with similar apparatus was undertaken in March of last year. This was completed and first put into operation the end of the following September, since which time it has been in continuous operation, with the exception of the latter half of December when changes were decided upon during whose carrying out it became necessary under the terms of the court decree to shut down the plant for a couple of weeks.

As was naturally to be expected many difficulties were encountered, some of which have already been entirely overcome while others are giving way more gradually before the systematic study of operating conditions.

Fig. 21 is a plan of the nine electrical precipitation units or chambers in their relation to the flue system and stack. It should here be noted that the two large fans indicated in the drawing are not required for the operation of the precipitating system nor to overcome any added resistance due to its introduction, as this latter is very slight indeed. The fans were made necessary by that section of the court's decree requiring dilution of the sulphur dioxide to three-quarters of a per cent. or less. When the furnaces are running on a high sulphur charge this feature of the decree necessitates a considerable dilution of the gases with fresh air and corresponding diminution of stack draft. At these times the fans are operated, but during a considerable portion of the time the sulphur dioxide in the gases can be brought low enough without interference with the draft, and during these periods the fans are stopped entirely although the gases still pass through them.

At the rectifier building the current is received from the companies' three-phase power circuit at 2300 volts,

¹ Clarence B. Sprague, U. S. Pats., 931,515, Aug. 17, 1909 and 984,498, Feb. 14, 1911. See also W. C. Ebaugh, *THIS JOURNAL*, 1, 686-9 (1909) and 2, 372-3 (1910).

60 cycles, and after being transformed up to from 25,000 to 30,000 volts under the control of the operator through variable resistance and induction regulators is rectified into an intermittent direct current as already explained and distributed to the individual precipitating units.

Fig. 22 shows a cross section through one of these units or precipitating flues as first installed. The double vertical lines represent the collecting or grounded electrodes each 6 inches wide by 10 feet high made of No. 10 sheet iron. The dotted lines represent the discharge electrodes consisting of two iron wire strands between which is twisted the discharge material, for which both asbestos and mica preparations have been used in this plant. Each unit contains 24 rows of 24 electrodes of each type. The collecting electrodes are carried by bars connected directly to the frame of the chambers themselves while the discharge electrodes are spanned by springs between a system of buss bars carried on externally placed insulators as shown in the figure. To the auxiliary chambers surrounding these insulators a small regulated amount of air is admitted to prevent conductive dust or fume from working back and settling on the insulators.

The cam and shaker rod extending across the middle of the unit was originally designed for the purpose of vigorously shaking the electrodes as it was greatly feared that the removal of precipitate from the electrodes in units of this size might be one of our most serious problems. In actual operation it has been found however that the electrodes can easily be shaken by hand from the top entirely free from dust, the whole operation including cutting the unit in and out of the system and the removal and replacement of its covers requiring only about ten minutes, and this having to be repeated every six or eight hours, depending on the dust content of the gases. The precipitated dust and fume as it falls from the electrodes is carried by the conveyor in each unit to a common longitudinal conveyor which in turn discharges into cars carrying it away for treatment and recovery of its values.

Fig. 23 is the interior of the rectifier house or control station showing the general arrangement of the apparatus and wiring. Fig. 24 shows the precipitation units in course of construction, while Fig. 25 is a view over the tops of six out of the nine units after completion. Figs. 26 and 27 are photographs of the main stack taken a few minutes apart with the electric current respectively off and on.

Filtration tests show that this plant under favorable working conditions precipitates between 80 and 90 per cent. of the suspended matter in the gas, the average over the whole period of operation to date being somewhat less. Under present operating conditions at the smelter this represents some 6 to 8 tons of precipitate per 24 hours. Fig. 28 shows this steady stream of precipitated smoke as it flows night and day from the end of the conveyor coming from the units.

The gas treating plant as a whole including flues fans, motors and electrical apparatus cost up to the

time it was first put in operation a little less than \$110,000. Although many minor changes have since been made none of the larger or more expensive elements of construction have been greatly altered.

The total average power consumption for the precipitation plant at present is in the neighborhood of 120 kws. One man can readily control the whole operation in the rectifier house although as a matter of precaution for a new plant under the high tension here used two have usually been on duty. Two laborers and a foreman are employed on the precipitating units and dust-handling system, although this can probably be reduced somewhat by automatic shaking devices, since as yet the main efforts at improvement have been directed elsewhere.

The volume of gases to be treated varies considerably with the conditions at the furnaces but at present may fairly be taken as averaging between 200,000 and 300,000 cubic feet per minute, and entering the units at from 100° to 150° C.

One of the greatest difficulties met with in this particular installation has been the maintenance of conductivity in the fine fibers of the asbestos and mica of the discharge electrodes. At ordinary room temperatures these materials readily take on enough moisture from the air to afford sufficient surface leakage for all the discharge necessary, and the same is true at higher temperatures if the gases contain traces of sulphuric acid or other conductive matter, but in the particular gases here met with the high and variable amount of zinc oxide at times robs them of all conductive matter, thus reducing the conductivity of the fibers of the electrodes and seriously effecting their efficiency. The possible methods of overcoming this and giving the fibers a permanent conductivity of their own as well as other details of the more purely electro-technical matters underlying the whole process will be treated more at length elsewhere as the present article is intended more as an outline sketch of the history and practical development of the work thus far accomplished. Nor is this the place to speculate upon the final outcome of situation between the farmers and the two great smelting plants which have adopted the remedial measures above described, for this is in the end a question for the botanical and agricultural expert, as to whether or not, or to what extent actual damage is still being done, no matter whether this comes from suspended matter or from the sulphur dioxide, which neither the bag house nor the electrical precipitation make any claim to remove. The two smelting companies have done and are doing everything in their power to better the conditions while on the other side the farmers, through the executive committee of their protective association, have earnestly tried to carry out their part in a spirit of fairness to all concerned.

To those who know the circumstances of the many bitter conflicts between farmers and smelters all over this country, with the attendant expense and usual barrenness of results, the present developments in Shasta County present a very suggestive illustration of what may be accomplished in the technical

development of our industries by spending the money on experiment and construction instead of all on litigation. Irrespective of the local issues involved the work done at both of these smelters during the past year has been a real and decided step forward in practical metallurgy. Both plants have already sufficiently demonstrated the applicability to large scale operation of the principles underlying them to ensure these principles finding a permanent place from now onward in the field of engineering, and each for the particular cases for which it is peculiarly adapted. Before us, of course, still looms the question of the sulphur dioxide and the solution for this on an equally large scale is unfortunately not yet clearly in sight.

Before leaving the subject I cannot but make grateful acknowledgment to those who have worked so earnestly and loyally shoulder to shoulder during the past year and to whose energy and ability such measure of success, as has been met with thus far, is entirely due. Especially do I wish to express appreciation of the courage, determination and ability of Mr. R. T. White, until recently general manager of the Balaklala Company, and now holding the corresponding post with the Braden Copper Company in Chili, in undertaking and carrying through this new developmental work with all its attendant risks under the most trying of circumstances. Fig. 29 is a snapshot of this staff at the works. From right to left on the back row they are: A. H. Trotter, chief engineer; H. R. Hollbrook, chemist; C. A. Van Amberg, master mechanic; R. B. Rathbun, chief electrician; R. House, chief operator precipitation plant; C. S. Hull, osillograph expert, General Electric Co.; and in the front row, from right to left: W. Eaton, engineer of tests; H. A. Burns, my own assistant and co-worker throughout all the work of the past four years; R. T. White, general manager; R. B. Green, smelter superintendent; and the author.

Of the other possible applications of the process, one of the most recent to be actively prosecuted is the collection of dust from Portland cement kiln gases. The chief stimulus to this development has again been the nuisance to the surrounding population and its attendant litigation. This has been especially acute in southern California where several cement plants are located in the heart of an exceedingly rich orange country. In the case of the Coulton plant with a capacity of 2500 barrels a day an injunction has already been issued by the court which, if sustained, will close the plant, unless they can control their dust which the court estimates at present at some 20 tons per day. This case differs from that of the smelters in that here there is no question of damage from gases but merely the deposition of a large tonnage of impalpable dust of lime and clay.

From the technical side a new condition is here met with in the high temperature of the gases to be treated, which are 450°C . and upwards as they leave the present stacks. The dust itself is furthermore entirely devoid of electrical conductivity, but notwithstanding this it is easily and completely precipi-

tated by the electrodes when these are properly adapted to the new conditions.

Experiments on a scale of a few hundred cubic feet per minute have been carried on for the past few months under the direction of Mr. Walter A. Schmidt, at the Riverside Portland Cement Works, and these have recently been extended to treat a good portion of the gases coming from one kiln. Fig. 30 represents this installation at its present stage. It is the intention after determining the most advantageous conditions for construction and operation on this kiln to equip the remaining seven kilns accordingly at which time a more complete description of the application of the process will be presented.

Another extensive field in which it is hoped this process may find useful application is the cleaning of iron blast furnace gas for use in gas engines. Outside of the poisonous and combustible nature of these gases and the consequent necessity for keeping the whole apparatus gas-tight there would appear to be no new difficulties here to overcome and steps are being taken to thoroughly test the matter on a practical scale, this work at present being in direct charge of Mr. L. L. Johnson, of Indianapolis.

A question which naturally presents itself is whether this work has any bearing upon the coal smoke problem of large cities. In answer it may be said that for the great majority of cases at present the more logical line of attack would seem to lie in improved methods of combustion, to avoid making smoke in the first place, but in some special instances where such methods may happen to be particularly difficult of application and the suppression of smoke is especially desirable, electrical precipitation may eventually be found of use, for experiments show that it acts upon ordinary smoke in essentially the same manner as upon the fumes and dust above discussed.

NOTE RECEIVED JULY 7, 1911.

Since the manuscript of the above article was sent to the printer the case of the Balaklala Company *versus* the Shasta farmers has come up for formal hearing in the United States Circuit Court in San Francisco, before Judge Morrow, on June 19th.

The evidence presented from the farmers' side consisted of a considerable number of affidavits from individual residents of the District in question, stating that they believed damage was still being done. They naturally made little or no attempt to distinguish between damage from gases and that from suspended matter. Of much more interest in the present connection was the report from Messrs. Gould and Burd, the chemists employed by the Shasta County Farmers' Protective Association, to examine the operating conditions at the Smelter itself and determine to what extent the terms of the decree were being fulfilled.

Their tests extended over the period from March 10th to April 3d and credit the electrical apparatus with removing during that period an average of 72.8 per cent. of the total solids in the gases entering it. In nearly one-third of the individual determinations the removal of solids reported is over 85 per cent.

They report the average concentration of sulphur

dioxide as 0.56 per cent. by volume, but state that several times during the month the concentration rose slightly above the 0.75 per cent. prescribed as maximum by the Court.

The outcome of the hearing was the entering of a judgment by agreement and stipulation between the contesting parties whereby the plant is allowed thirty-five days under existing conditions in which to run through the ore on hand, but is then required to close down completely until such time as it can live up to the letter of the original decree, *viz.*, remove *all* solids, never exceed 0.75 per cent. sulphur dioxide and do no damage.

During the time in which the plant still remains in operation experimentation and development is being carried on as vigorously as ever, but it is scarcely expected even under the most favorable conditions that a shut-down can be entirely avoided. During such shut-down, however, the progress of the work at other plants already undertaken thoroughly insures the uninterrupted development of the process in general.

PAPER-MAKERS' CLAYS.

By J. STEWART REMINGTON, DOUGLAS A. BOWACK AND PERCY DAVIDSON.

Received April 17, 1911.

The commercial value of a china clay for use as a loading material depends largely upon the whiteness of the body, and essentially its freedom from grit and sand. For example, should "fillers" be used which contain more gritty matter than is desirable in a china clay, the detrimental effects on the machinery will be quickly noticed, more especially when the wear and tear of the wires is taken into consideration.

latter, especially the compounds containing iron, exercise a great influence on the color of the natural clay, and it is therefore imperative that the fullest use should be made of information gathered from a chemical analysis. The iron exists chiefly in the form of ferric oxide (hydrated), ferrous carbonate (siderite), ferric sulphide (pyrites) and occasionally as ferric silicates. Hence, although the actual figures found for iron on the analysis of any two samples may correspond, it is known that deposits vary so much in their physical and chemical properties that the percentage of iron is not a direct criterion of the value of a china clay for paper-making purposes.

It is not, therefore, sufficient that merely the amount of each constituent of clay be ascertained: information is required as to the various proportions of true kaolin, silt, sand and gritty particles present, and also the state of fineness of the sample. The foregoing is best obtained by mechanical analysis, the principle of which consists in carefully and systematically washing the clay in an apparatus specially devised for the purpose, whereby the lighter "true-clay" substance is readily washed away from the larger and heavier constituents. Moreover, if desirable, the residual matter may be microscopically examined in order to ascertain the exact nature of the different minerals in the clay.

To obtain evidence as to the nature of the various clay deposits in England it is necessary to compare the composition, color and fineness of the best known brands, and with this object in view the following summaries have been prepared from a selection of analyses and reports, made by the authors to the interests of paper manufacturers concerned:

TABLE AND RESULTS OF THE PRACTICAL INVESTIGATIONS.

Analyses: Chemical Constituents.

No. of clay.	Silica. SiO ₂ .	Alumina. Al ₂ O ₃ .	Ferric oxide. Fe ₂ O ₃ .	Lime. CaO.	Magnesia. MgO.	Total water.	Alkalies. K ₂ O.	Total.	Order of merit.	Residue, per cent., Standard grit test.	Nos. fineness, etc. Order of merit in:	Suitable uses for:
1	46.21	39.82	0.38	0.45	0.10	12.81	0.23	100.00	A	0.09	100	Coating papers
2	46.32	39.76	0.40	0.41	0.11	12.69	0.31	100.00	B	0.07	100	Coating papers
3	47.60	38.26	0.55	0.42	0.20	12.40	0.57	100.00	C	0.32	95	High-grade papers
4	47.74	37.66	0.58	0.61	0.22	12.60	0.59	100.00	D	2.96	75	News
5	45.74	36.84	1.86	0.60	0.11	11.06	3.79	100.00	B	0.24	85	High-grade papers and coating papers
6	46.46	37.40	2.00	0.86	0.21	11.81	1.26	100.00	A	2.22	70	News
7	48.16	38.45	2.06	0.50	0.14	10.59	0.10	100.00	D	3.90	65	Cheaper loadings and news
8	46.20	36.23	1.57	0.76	0.11	11.00	4.13	100.00	C	4.10	65	Cheaper loadings and news
9	46.60	37.48	1.26	0.64	0.22	12.74	1.06	100.00	C	1.19	90	High-grade papers
10	46.28	38.38	1.03	0.72	0.15	12.87	0.66	100.00	B	1.30	90	High-grade papers
11	46.38	39.00	0.79	0.58	0.11	12.70	0.44	100.00	C	1.00	90	High-grade papers
12	47.26	37.84	1.08	0.54	0.29	12.07	0.82	100.00	D	2.35	75	News
13	46.12	38.80	1.08	0.82	0.15	12.62	0.41	100.00	D	1.15	90	High-grade papers
14	46.90	38.53	1.01	0.76	0.11	12.49	0.20	100.00	C	0.61	90	High-grade papers and coating papers
15	46.86	39.24	0.75	0.61	0.15	12.24	0.15	100.00	A	0.77	90	High-grade papers and coating papers
16	46.62	38.98	0.81	0.69	0.10	12.30	0.50	100.00	B	0.98	90	High-grade papers
17	45.92	38.43	0.71	1.18	0.21	12.77	0.78	100.00	A	2.28	75	Ordinary white printings
18	44.82	38.69	1.30	0.94	0.20	12.79	1.26	100.00	B	2.10	75	Ordinary white printings
19	46.74	37.87	0.89	0.50	0.24	12.44	1.36	100.00	B	0.93	90	High-grade papers
20	46.76	38.06	0.86	0.82	0.20	12.01	1.29	100.00	A	1.12	90	High-grade papers

The coloration of the clay, which is of the greatest importance, is due partly to organic matter and partly to the various minerals contained in the clay. The

The results of the investigation of this representative list of clays point to the conclusion that these products are of first-rate commercial value, and com-

pared with corresponding figures furnished by some other good specimens of clays previously examined, the opinion formed is that many of them could hardly be surpassed in purity and quality. An important and interesting fact will be at once noted regarding the relative values of these deposits; *viz.*, with a few exceptions the specimens are remarkably uniform in character and on the whole may be considered as representing a high standard of perfection now reached in the progress of a great industry.

On comparing the figures of the clays marked No. 6 to No. 8, with those yielded by the samples obtained from other deposits, it is evident that there is a great difference in the proportion of iron contained in these minerals. A corresponding difference appears in the general character of the clays, notably when compared with those marked Nos. 1 to 4, and those marked Nos. 9 to 12, which are finer and possess a much better color. The latter variation may be partly owing to a difference in the nature and extent of the surrounding beds, or to some local circumstances affecting the cleaning of the material and the nature of the clay produced. The presence of a comparatively high percentage of alkalis in the clays Nos. 5 and 8 points to the fact that the clay is associated with an unusually large quantity of unaltered feldspar and some micas, while the potash content found on analysis indicates the presence of "muscovite," one of the characteristic minerals of the crystalline rocks, granites, etc. This information leads one to suppose that the clay has been mined near some point of gradation of the true kaolin and the primary bed: a corresponding increase of the constituents of the original rock is noticed, which serves to confirm this impression.

With regard to the question of the properties imparted to papers by the use of different kinds of fillers, one can hardly differentiate between values of the best qualities: at least, when dealing with high-class grades, such as the above mentioned. One might go further, however, and say that more attention should be given by consumers to the question of the state of fineness of the clays acquired for the purpose of loading. For example, clays are not uncommonly found on the market which to all intents and purposes are equal in purity and color to the well-known brands of standard clays, but, on a physical examination, they are proved to contain as much as 8 to 12 per cent. of grit, and sometimes even 18 per cent. Again, the question of difference in price is often very little, the rate being but slightly lower than that demanded for really high-grade material.

It will be readily understood from this digression that the absolute analytical figures, unless interpreted by a skilled chemist, do not accurately gauge the entire value of the clay, because the component parts of the foreign débris, usually associated with clay, bears a close relationship to the ratio of the constituent elements in the true kaolin itself. It behooves buyers, therefore, to attach due importance to the classification which is based on the composition fur-

nished under this system of mechanical separation of the gritty particles.

AYNSOME TECHNICAL LABORATORIES
LANCASHIRE, ENGLAND

A SCHEME FOR THE RAPID ANALYSIS OF CEMENT.

BY CLAUDE N. WILEY AND W. A. LESTER

Received June 15, 1911.

Chemists who are engaged in the manufacture or testing of Portland cement have long wished that they could obtain a complete analysis of a cement, the composition of which was in question, without proceeding with the tedious and lengthy method generally employed. This method, in order to be accurate, calls for the solution of the cement in HCl, evaporation to dryness, followed by a short baking in order to render the silicic acid entirely dehydrated and insoluble. This evaporation must be carried out with more or less care, because if the evaporation is made at too great a temperature or in too hasty a manner, and extreme care is not taken, the gelatinous silicic acid, in being freed from its water, will spatter and danger of loss is incurred. The operation requires at best from three to four hours, and if all of the silicic acid is not dehydrated, a loss is bound to occur through silica passing through the filter.

The old method for the separation of iron and alumina, by means of fusion with potassium acid sulphate, is also a source of annoyance to the busy chemist. Fusion must be carefully watched until the liquid stage has been reached, and even then, if the heat is not carefully adjusted, frothing or boiling over is frequent. To make this fusion requires time and attention taken from other, perhaps more important, work. The solution of the cake is again an occasion of delay and the reduction of the iron present, to be properly accomplished, requires several hours and, if the iron is in large quantity, even longer.

The determination for magnesia also consumes much time and it is the general custom to allow the granular crystalline precipitate of magnesium ammonium phosphate to completely subside so that filtration may be speedily accomplished.

A complete analysis of cement, therefore, covers a period of two days' time, although it can be done in the course of one day by careful manipulation. The authors have been searching for some time to find a method whereby accurate results could be obtained in a much shorter time. They had already adopted the schemes for the determination of magnesia and the separation of iron and alumina, which will be described later, but had found no suitable method for the rapid accurate determination of silica.

Some time ago there appeared in *Tonindustrie Zeitung*, 35, 265, a method described by C. Hentschel, whereby silica can be accurately separated from cement by means of acetic acid and in a very short time. Here, at last, appeared the solution of our problem, and upon the first trial of this method we knew that the operation of cement analysis could be accomplished in a few hours' time.

The method described by Hentschel is as follows:

"One gram of cement is ground to powder in a porcelain dish; a little water and 10 cc. acetic acid are added. The mixture is then heated under constant stirring for about 15-20 minutes, till the cement has settled and no particles are floating around any more. Now more distilled water and as much dilute HNO_3 are added as is necessary to keep the iron and the silicates of aluminum in solution. The mixture is heated again for 5 minutes. It is then filtered off with accompanying decantation of the residue silica, washed in hot water and filtered again. If sufficient care is taken, the filtered silica will always be free from iron and aluminum silicates. After washing the silica is ignited and then weighed. After heating in the water bath, the solution must be treated with HNO_3 and not HCl , as this would prolong the test. The determination can be made within one and one-fourth hours, whereas any of the other methods take at least 3 to 4 hours."

After repeated trials, the authors have decided that there is no difference in the time of operation, whether HNO_3 or HCl be added to the liquid after solution by acetic acid. Also, it has been determined that but 5-6 minutes are required for digestion if 0.5 gram of material is used and the results on the smaller amount are equally accurate.

The entire method for the complete analysis of Portland cement now in use by the writers is as follows: Weigh 0.5 gram of cement into a porcelain casserole, add water and then 10 cc. glacial acetic acid. Stir with a glass rod until all lumps are broken up, then place on the hot plate and digest, stirring from time to time until no particles of cement remain. This requires about 5 minutes, and care should be taken that the contents do not boil over. To this solution add a dilute solution of HCl until the reddish color is dissipated. Filter and wash thoroughly with hot water, ignite the precipitate, blast for a few minutes, cool and weigh. After a little experience this operation can be completed in 30 minutes.

The filtrate from the silica is now made up to 200 cc. in a graduated flask and aliquot portions separated. To the first is added a few drops of HNO_3 and then NH_4OH until the iron and alumina are precipitated as hydrates. Set the solution aside for a few minutes on the hot plate until subsidence takes place, filter, wash, ignite and weigh as oxids. Alumina and iron are separated in the second portion by means of the Zimmermann-Reinhardt method. Heat the solution to boiling, reduce the ferric chlorid by adding, drop by drop, a solution of stannous chlorid¹ until the solution becomes colorless. Cool, make up to 300 cc., and add 25 cc. MnSO_4 solution.² Stir vigorously, add 10 cc. HgCl_2 (saturated solution) and titrate the solution at once with KMnO_4 .

The filtrate from the first portion is now made up to about 400 cc., the lime precipitated at $\text{Ca}_2\text{C}_2\text{O}_4$.

¹ Stannous chlorid solution: 25 grams stannous chlorid are dissolved in 100 cc. concentrated HCl and diluted with water to 1 liter.

² MnSO_4 solution: 67 grams crystalline $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ are dissolved in 500-600 cc. water, 138 cc. phosphoric acid (sp. gr. 1.70) and 130 cc. concentrated sulfuric acid (sp. gr. 1.82) are added and the mixture diluted to 1 liter.

filtered, washed and titrated with KMnO_4 in the usual manner.

The filtrate from the lime is boiled down in an evaporating dish to about 200 cc., acidified with HCl and washed into an Erlenmeyer flask. Add sodium ammonium phosphate solution and about 5 cc. NH_4OH and cool in running water, shaking vigorously, until the precipitate begins to form. Then add about 15 cc. of NH_4OH and shake for about 10 minutes. Allow the precipitate to settle for about 5 minutes and filter. Wash with the usual solution, ignite and weigh as $\text{Mg}_2\text{P}_2\text{O}_7$.

While the above procedure has been carried on, another sample has been started for the determination of sulphuric anhydride. In this case take 1 gram of cement, digest with acetic acid as before, and add dilute HCl before filtering. The filtrate is heated to boiling and a few cc. of alcohol are added. BaSO_4 is precipitated by means of BaCl_2 solution and the beaker stood on the hot plate for one-half hour, at the end of which time all of the BaSO_4 will have subsided and filtration can be speedily accomplished.

From a large number of determinations we have found that it requires from 2 to 2.5 hours to make a complete analysis of cement and our results have agreed very closely with those obtained by means of the usual method. These results are sufficiently accurate for control work and the great saving in time makes this short method of much value. In the routine of the cement works laboratory, the daily analysis of the finished cement becomes very monotonous because of the fact that it may be considered "post-mortem" work, by which is meant that the composition of the cement cannot now be altered. Where large clinker storages are in use, the clinker may not be ground for several weeks after it is discharged from the kilns. It is thus seen that analysis of the finished cement is of very little value except for purpose of record and comparison with the physical tests.

Following are given several results of analyses made by both methods:

	Regular.			Acetic acid.		
	(1)	(2)	(3)	(1)	(2)	(3)
SiO_2	21.42	22.74	21.50	21.34	22.94	21.40
Al_2O_3	7.38	7.24	7.66	7.34	6.98	7.56
Fe_2O_3	2.60	2.72	2.84	2.60	2.72	2.84
CaO	62.40	61.46	62.18	62.40	61.85	62.33
MgO	2.41	2.26	2.51	2.52	2.26	2.45
SO_3	1.33	1.45	1.27	1.34	1.45	1.27
Ig. loss.....	1.54	1.38	1.14	1.54	1.38	1.14

Nos. 1 and 3 were completed in 2.5 hours and in No. 2 the SiO_2 , R_2O_3 and CaO results were obtained in 45 minutes after the sample was weighed. We have obtained results of complete analyses which have checked closer than the above, but these are given as they represent the average of our experience. Determinations of SiO_2 completed in 20 minutes check as follows with SiO_2 evaporations:

	Regular.			Acetic acid.		
	(1)	(2)	(3)	(1)	(2)	(3)
	21.54	22.94	21.56	21.50	23.00	21.65

Efforts have been made to apply this acetic acid scheme for the decomposition of raw material, shale and clay, and limestone, but so far have not been successful. Evaporation after fusion must be practiced to render the silica insoluble, but it is our hope to find a method whereby this determination may be considerably shortened.

LABORATORY OF THE
ATLANTIC & GULF PORTLAND CEMENT CO.,
RAGLAND, ALA.

THE DETERMINATION OF SULPHUR IN COAL BY MEANS OF JACKSON'S CANDLE TURBIDIMETER.

By HENRY F. MUEER.

Received May 5, 1911.

The candle turbidimeter is an apparatus originally devised by D. D. Jackson for the purpose of measuring the turbidity of water, and thereby furnishing a means of comparing different waters in that respect.¹ The simplicity and ease of operation of this apparatus led to its adoption as a standard for that purpose.² Further experiments demonstrated the possibility of calibrating the apparatus for measuring the turbidity produced by certain precipitates, such as barium sulphate and calcium oxalate, thus indicating the amount of sulphate, or lime, present in the tested solution. Tables of values were prepared and the apparatus was adopted by the U. S. Geological Survey for use in the field assay of water.³

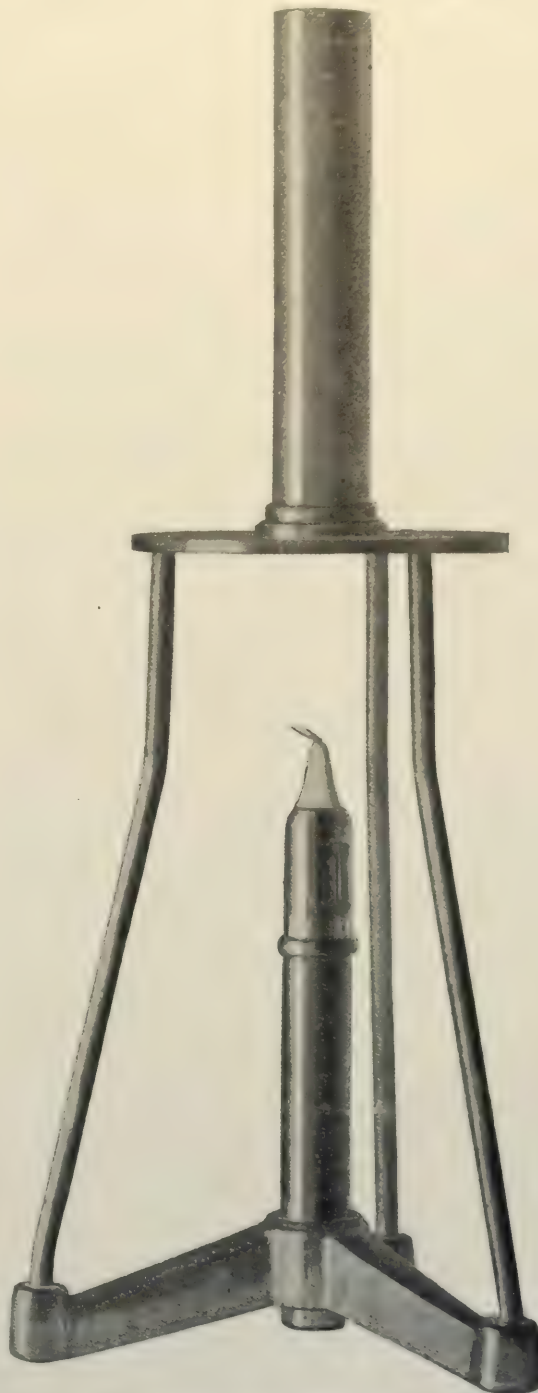
The apparatus comprises a support for a standard candle, in which the candle is kept at a constant height by means of a spring. This is set upright in a base, to which is attached the support for the removable holder of the graduated tube used to measure the depth of the turbid solution necessary to efface the image of the candle flame. Naturally, the more turbid the liquid, the less will be required to efface the image of the flame.

Although the results obtained photometrically cannot be expected to show the same exactness as the gravimetric methods, such an apparatus will, if properly used, give very satisfactory results, and is especially advantageous in routine work when large numbers of samples have to be examined daily and rapidly. Such a case is the determination of "volatile" sulphur in coal. By means of the bomb calorimeter and the candle turbidimeter this may be determined in about ten minutes, whereas by the gravimetric method the result would not be obtained in less than two hours. This apparatus is equally useful in the routine determination of the SO_2 content of cements and boiler waters.

When the writer began the use of the candle turbidimeter in routine coal work it was deemed desirable to make frequent gravimetric check determinations in order to note possible errors. In the course of these control tests it was found that the results obtained with the turbidimeter did not always correspond with the gravimetric results. The differ-

ences seemed greater than was desirable, and an investigation was begun in order to learn the cause.

A re-standardization of Jackson's table was first attempted. For this purpose a sodium sulphate solution was prepared and carefully standardized gravimetrically. It was of such a strength that 1



Jackson's candle turbidimeter.

cubic centimeter contained 1 milligram of sulphur, or 4.43 milligrams of sodium sulphate. The flasks and burettes chosen were all in agreement with each other, but when aliquot parts of the sulphate solution were acidified and diluted to 100 cubic centimeters, and tested with the turbidimeter, it was

¹ *Techn. Quarterly*, **13**, 278 (1900).

² *Stand. Meth. Water Anal.*, Am. Pub. Health Assn., 1905.

³ *U. S. Geol. Sur. W. S. Paper* **151**, 1905.

found that the results did not at all points agree with the original table of sulphur values published by Jackson,¹ and that the results obtained at different times were not consistent. The study was then continued in order to ascertain the reasons for the variations and inconsistencies.

The effect of variations in the candle flame was first investigated. A millimeter scale was attached to the candle support in such a way that the length of the flame could be read off directly. Beginning with a flame 20 millimeters long, the increase in length was found to be at the rate of 3 millimeters every two minutes up to a maximum of 50 to 55 millimeters. The variations in the results caused by these differences in the length of the flame were entirely negligible, being much less than the errors normal to the apparatus. It follows from the above, and was proven by experiments, that the distance of 3 inches between the top of the candle tube and the bottom of the glass tube may be varied considerably without causing an appreciable error. It is desirable, however, to adjust the candle tube so that the distance will be constant, in order to ensure the maintenance of the same conditions in all determinations.

Hydrochloric acid in large excess was found to cause low results with weak sulphate solutions. Some free hydrochloric acid is necessary, however, in order to give a precipitate suitable for reading in the turbidimeter. Neutral sulphate solutions, when precipitated with barium chloride, form a precipitate which is coarse and irregular, whereas the precipitate in a sulphate solution which has been slightly acidified with hydrochloric acid is very fine and of uniform texture. When using aliquot parts of a neutral sulphate solution, the acid should not be added until the portion taken has been diluted nearly to 100 cubic centimeters and well mixed. Failure to observe this precaution was found to be coincident with variable results.

The discrepancies between the turbidimetric and gravimetric results in the case of the coal solutions were at first thought to be caused by the presence of nitrates in the solutions examined. The disturbing effect of these in gravimetric sulphur determinations has frequently been noted.² The presence of nitrates in the solutions, in amounts equal to or exceeding the sodium sulphate present, was found to cause slightly high results in the turbidimetric estimation of the sulphur. The error thus caused, however, is too small to be taken into account.

The principal cause of the variations noted was found to be the difference in size and hardness of the barium chloride crystals used for the precipitation of the sulphur. It appears that the texture of the barium sulphate resulting from cold precipitation is very much affected by the rate at which it is formed in the solution, and will be the finer the more slowly it is formed, and *vice versa*. Hence large crystals of barium chloride which dissolve more slowly form a barium sulphate of finer texture, which, when sus-

pended in the liquid, will efface the image of the flame much sooner than a coarser one more rapidly formed. This was actually found to be the case, and the regularity of this effect is well shown by the following table:

TABLE I.—EFFECT OF DIFFERENT SIZES OF BARIUM CHLORIDE CRYSTALS.

Data:

Solution—100 cc. contained 10 mg. sulphur.

Barium chloride used for each test—2 grams.

The size of the barium chloride is that remaining successively on each sieve of the series as numbered.

Size sieve.	Reading. Cm.	Size sieve.	Reading. Cm.	Size sieve.	Reading. Cm.
2	2.1	16	3.5	36	3.8
4	2.2	20	3.5	40	4.3
8	2.4	24	3.5	50	4.5
10	2.6	30	3.7	60	4.5
				100	4.6

The sieves used in sizing the barium chloride for the above tests were the standard sieves used in mechanical analysis of sand, except numbers 2, 4, and 8, which were made from wire screening. Since all of the above tests were made on the same solution, it will be noted that the error due to the difference in the size of the barium chloride is considerable.

It was also found that in the case of the smaller sizes of barium chloride differences in manipulation made rather large differences in the readings. The variations in the results were greater the smaller the barium chloride crystals used. The following is a case in point:

The solution used contained 10 milligrams of sulphur in 100 cc.; the barium chloride used was of sieve size 30. When the solution was placed in a glass-stoppered bottle and shaken after adding the barium chloride, the resulting reading was 3.8 centimeters. But when the solution was placed in a beaker, the barium chloride added, and the mixture poured back and forth into another beaker until the barium chloride was dissolved, the reading was 2.8 centimeters. It is evident, therefore, that in photometric sulphur work it is necessary to adhere strictly to the prescribed procedure.

In view of the above observations many attempts were made to obtain a barium chloride of a standard size which might be duplicated at any time. Although the screening out of any particular size presented no difficulty, the results obtained from different lots of the salt were not as concordant as was desired. Several experiments indicated that this was apparently due to varying hardness and efflorescence of the crystals, whereby the rate of solubility was much affected.

In order to eliminate the errors caused by the varying physical properties of the barium chloride, solutions of the salt were prepared and used in further tests. It was then found that with a concentrated solution of barium chloride the range of the table was materially altered. If a solution contained more than 10 milligrams of sulphur in 100 cubic centimeters, the solution required to be diluted to 200 cubic centimeters in order to obtain a precipitate of sufficiently fine texture to produce a distinct end point. The lower part of the table, however, was

¹ J. Am. Chem. Soc., **33**, 799.

² *Ibid.*, **31**, 55 (1909); **32**, 613 (1910); Chem. Abs., **3**, 1623; THIS JOURNAL, **2**, 199 (1910).

not greatly affected. But the precipitate produced by the solution of barium chloride was in all cases coarser and more irregular in texture than that obtained by means of solid barium chloride.

The addition of a small amount of oxalic acid¹ to the barium chloride solution effected a considerable improvement in the character of the precipitate, rendering it much finer, and made it possible to obtain a direct reading in one operation from a solution containing as low as 1 milligram of sulphur in 100 cubic centimeters. With such a precipitating solution it was found possible, within a limited range, to reproduce given results at any time, provided the method were followed exactly. As in the case of solid barium chloride, differences in the method of manipulation gave different results, but by no means as great as before.

The same was true of variations in the amount of free hydrochloric acid in the sulphate solution. If much more than the prescribed amount of free hydrochloric acid was present, it caused low results, the magnitude of the error depending upon the proportion of the excess of acid to the concentration of the sulphate solution. An excess of oxalic acid, however, caused high results, the extent of which also depended on the excess of acid and the concentration of the sulphate solution. The general effect of the oxalic acid was to contract the table, especially in the lower values.

It was found, however, that a barium chloride-oxalic acid solution of a given formula would not answer for the entire range of the table. A solution which gave good results in the lower values would not do for the higher ones. In fact, it was almost impossible to obtain a good precipitate beyond the 5-milligram point. The precipitate formed by means of a solution of barium chloride was formed so rapidly that it was very coarse, and the effect of the oxalic acid was gradually lessened as the strength of the sulphate solution increased. This was also partly due to the fact that as the oxalic acid content of such a precipitating solution increased, it required increased amounts of free hydrochloric acid to prevent separation of barium oxalate. Beyond a certain point these two acids neutralized one another so far as their effect on the barium sulphate formation was concerned; hence the result was practically the same as when using a simple barium chloride solution.

The best, most regular, and most accurate results were finally obtained by the use of barium chloride in the form of tablets² weighing 1 gram each, compressed without the use of a binder. The advantages of using barium chloride in this form are: convenience in handling, and the certainty of having a uniform weight and volume of the precipitant in each test. By this means the variations in results due to the differences in the size and hardness of the barium chloride crystals are practically eliminated. The precipitate produced by means of these tablets is uniform and gives a good end point for all parts of the table. The table obtained by means of these

TABLE II. TURBIDIMETRIC SULPHUR TABLE.

For use with Jackson's candle turbidimeter.
Sulphur and SO₃ contained in 100 cc. precipitated.

Depth Cm.	S. Mg.	SO ₃ Mg.	Depth. Cm.	S. Mg.	SO ₃ Mg.	Depth. Cm.	S Mg.	SO ₃ Mg.
1.0	20.0	50.0	9.1	2.28	5.70	17.1	1.49	3.73
1.1	18.0	45.0	9.2	2.26	5.65	17.2	1.49	3.73
1.2	16.5	41.3	9.3	2.25	5.63	17.3	1.48	3.70
1.3	15.0	37.5	9.4	2.23	5.58	17.4	1.47	3.68
1.4	13.5	33.8	9.5	2.21	5.53	17.5	1.47	3.68
1.5	12.5	31.3	9.6	2.19	5.48	17.6	1.46	3.65
1.6	11.2	28.0	9.7	2.18	5.45	17.7	1.45	3.63
1.7	10.0	25.0	9.8	2.16	5.40	17.8	1.44	3.60
1.8	9.5	23.8	9.9	2.15	5.38	17.9	1.44	3.60
1.9	9.0	22.5	10.0	2.13	5.33	18.0	1.43	3.58
2.0	8.5	21.3	10.1	2.11	5.28	18.1	1.43	3.58
2.1	8.0	20.0	10.2	2.10	5.25	18.2	1.42	3.55
2.2	7.6	19.0	10.3	2.09	5.23	18.3	1.41	3.53
2.3	7.3	18.3	10.4	2.07	5.18	18.4	1.41	3.53
2.4	7.0	17.5	10.5	2.06	5.15	18.5	1.40	3.50
2.5	6.7	16.8	10.6	2.04	5.10	18.6	1.40	3.50
2.6	6.5	16.3	10.7	2.03	5.08	18.7	1.39	3.48
2.7	6.3	15.8	10.8	2.02	5.05	18.8	1.38	3.45
2.8	6.1	15.3	10.9	2.01	5.03	18.9	1.38	3.45
2.9	5.9	14.8	11.0	2.00	5.00	19.0	1.37	3.43
3.0	5.7	14.3	11.1	1.98	4.95	19.1	1.37	3.43
3.1	5.5	13.8	11.2	1.97	4.93	19.2	1.36	3.40
3.2	5.4	13.5	11.3	1.95	4.88	19.3	1.35	3.38
3.3	5.2	13.0	11.4	1.94	4.85	19.4	1.35	3.38
3.4	5.1	12.8	11.5	1.93	4.83	19.5	1.34	3.35
3.5	5.0	12.5	11.6	1.92	4.80	19.6	1.34	3.35
3.6	4.85	12.25	11.7	1.91	4.78	19.7	1.33	3.33
3.7	4.75	12.00	11.8	1.90	4.75	19.8	1.32	3.30
3.8	4.63	11.75	11.9	1.89	4.73	19.9	1.32	3.30
3.9	4.52	11.50	12.0	1.88	4.70	20.0	1.31	3.28
4.0	4.43	11.25	12.1	1.87	4.68	20.1	1.30	3.25
4.1	4.33	11.00	12.2	1.86	4.65	20.2	1.30	3.25
4.2	4.24	10.75	12.3	1.85	4.63	20.3	1.29	3.23
4.3	4.16	10.50	12.4	1.84	4.60	20.4	1.28	3.20
4.4	4.08	10.25	12.5	1.83	4.58	20.5	1.28	3.20
4.5	4.00	10.00	12.6	1.82	4.55	20.6	1.27	3.18
4.6	3.93	9.83	12.7	1.81	4.53	20.7	1.26	3.15
4.7	3.86	9.65	12.8	1.80	4.50	20.8	1.26	3.15
4.8	3.79	9.48	12.9	1.79	4.48	20.9	1.25	3.13
4.9	3.72	9.30	13.0	1.78	4.45	21.0	1.25	3.13
5.0	3.66	9.15	13.1	1.77	4.43	21.1	1.24	3.10
5.1	3.60	9.00	13.2	1.76	4.40	21.2	1.23	3.08
5.2	3.54	8.85	13.3	1.75	4.38	21.3	1.23	3.08
5.3	3.49	8.73	13.4	1.74	4.35	21.4	1.22	3.05
5.4	3.43	8.58	13.5	1.73	4.33	21.5	1.21	3.03
5.5	3.38	8.45	13.6	1.73	4.33	21.6	1.21	3.03
5.6	3.33	8.33	13.7	1.72	4.30	21.7	1.20	3.00
5.7	3.28	8.20	13.8	1.71	4.28	21.8	1.20	3.00
5.8	3.24	8.10	13.9	1.70	4.25	21.9	1.19	2.98
5.9	3.20	8.00	14.0	1.70	4.25	22.0	1.18	2.95
6.0	3.15	7.88	14.1	1.69	4.23	22.1	1.18	2.95
6.1	3.11	7.78	14.2	1.68	4.20	22.2	1.17	2.93
6.2	3.07	7.68	14.3	1.67	4.18	22.3	1.16	2.90
6.3	3.03	7.58	14.4	1.66	4.15	22.4	1.16	2.90
6.4	2.99	7.48	14.5	1.66	4.15	22.5	1.15	2.88
6.5	2.95	7.38	14.6	1.65	4.13	22.6	1.15	2.88
6.6	2.92	7.30	14.7	1.64	4.10	22.7	1.14	2.85
6.7	2.88	7.20	14.8	1.63	4.08	22.8	1.13	2.83
6.8	2.85	7.13	14.9	1.62	4.05	22.9	1.13	2.83
6.9	2.82	7.05	15.0	1.62	4.05	23.0	1.12	2.80
7.0	2.79	6.98	15.1	1.61	4.03	23.1	1.11	2.78
7.1	2.76	6.90	15.2	1.60	4.00	23.2	1.11	2.78
7.2	2.73	6.83	15.3	1.60	4.00	23.3	1.10	2.75
7.3	2.70	6.75	15.4	1.59	3.98	23.4	1.09	2.73
7.4	2.67	6.68	15.5	1.59	3.98	23.5	1.08	2.70
7.5	2.64	6.60	15.6	1.58	3.95	23.6	1.08	2.70
7.6	2.61	6.53	15.7	1.57	3.93	23.7	1.07	2.68
7.7	2.59	6.48	15.8	1.57	3.93	23.8	1.06	2.65
7.8	2.56	6.40	15.9	1.56	3.90	23.9	1.05	2.63
7.9	2.54	6.35	16.0	1.56	3.90	24.0	1.05	2.63
8.0	2.51	6.28	16.1	1.55	3.88	24.1	1.04	2.60
8.1	2.49	6.23	16.2	1.54	3.85	24.2	1.03	2.58
8.2	2.47	6.18	16.3	1.54	3.85	24.3	1.03	2.58
8.3	2.44	6.10	16.4	1.53	3.83	24.4	1.02	2.55
8.4	2.42	6.05	16.5	1.53	3.83	24.5	1.02	2.55
8.5	2.40	6.00	16.6	1.52	3.80	24.6	1.01	2.53
8.6	2.38	5.95	16.7	1.52	3.80	24.7	1.01	2.53
8.7	2.36	5.90	16.8	1.51	3.78	24.8	1.00	2.50
8.8	2.34	5.85	16.9	1.50	3.75	24.9	1.00	2.50
8.9	2.32	5.80	17.0	1.50	3.75	25.0	1.00	2.50
9.0	2.30	5.75						

¹ THIS JOURNAL, 1, 690.

² These tablets were prepared on order by the Fraser Tablet Co., of Brooklyn, N. Y.

tablets is somewhat different from that originally published by Jackson and is given above.

The method of operation used in the preparation of this table, and which should be used in all determinations by means of this apparatus, is as follows:

The aliquot of the solution to be tested is measured into the turbidimeter tube, diluted to near the 100 cc. mark, shaken, then acidified with 1 cc. of 1:1 hydrochloric acid, made up to the mark, and mixed well by shaking. One of the barium chloride tablets¹ is then dropped in and the tube closed by means of a clean rubber stopper. The tube is then tilted up and down, causing the tablet to roll back and forth through the solution by gravity.

When the precipitation appears to be complete, the remainder of the tablet may be dissolved by rapidly rotating the tube; but violent shaking should be avoided, since it would have a tendency to cause aggregation of the precipitate. The turbid liquid is then transferred to a beaker, the candle lighted, a small quantity of the liquid poured into the glass tube to prevent overheating and cracking, and the tube put in place. More of the liquid is then poured in, allowing it to run down the side of the tube, rapidly at first, until the image of the flame becomes dim, then more slowly, waiting a moment after each addition until the liquid in the tube is quiet, and continuing thus until the image of the flame just disappears. The depth of the liquid in centimeters is noted. The mixture is then returned to the beaker, poured back and forth from beaker to tube two or three times, and read again as before.

Having thus obtained empirically a set of readings corresponding to sulphate solutions of graded strength, the relation between these values was made the subject of study. The weights of barium sulphate contained in each volume of liquid obscuring the flame at the determined points were plotted as abscissas against the centimeters depth of the liquid as ordinates, and it was found that between the 2.5 centimeter and the 17.0 centimeter marks these weights formed a practically straight line. Between these two points the amount of barium sulphate required to obscure the flame increases slightly and is directly proportional to the depth of liquid. From this line the following formula was deduced:

$$S = 0.6 + \frac{15.3}{C}$$

where S is the amount of sulphur, in milligrams, and C is the depth in centimeters of the turbid liquid, between 2.5 cm. and 17.0 cm.

Below the 2.5 cm. mark there was a sudden and sharp deviation of the line, showing that the amount of barium sulphate required to hide the flame below this point increased rapidly in *inverse* proportion to the depth, a condition opposite to that previously described. This is probably due to the fact that the bottom of the turbidimeter tube forms a lens, whose

focus is probably at or near the 2.5 cm. mark on the tube. This lens effect will also explain why variations in the size of the flame make no appreciable difference in the results, as previously shown, since the image of the flame will always be focused at the 2.5 cm. mark, no matter what its size may be. The readings below the 2.5 cm. mark are also complicated by the fact that the solutions whose readings fall below this point are so strong that they form a dense precipitate which settles rapidly. Above the 17.0 cm. mark the amount of barium sulphate required to hide the flame becomes gradually less. The decrease is, however, very slight for the remainder of the tube.

By means of the above information the values of the Turbidimetric Sulphur Table were all co-ordinated. The accuracy of this table is shown by the conformity of results obtained by precipitating varying amounts of the same solution (see Table III). These results were obtained in routine analysis of coal by the writer, and by Messrs. C. B. Phipps and J. A. Powders, chemists of this laboratory.

TABLE III.—COMPARISON OF TURBIDIMETRIC AND GRAVIMETRIC RESULTS ON VARIOUS COAL SOLUTIONS.

Test No.	Aliquot taken.	Turb. reading. Cm.	Turb. sulphur. Per cent.	Grav. sulphur. Per cent.
1.....	1/4	10.5	0.82	0.86
2.....	1/4	5.1	1.44	1.40
3.....	1/4	1.7	4.00	
	1/10	4.5	4.00	4.03
4.....	1/4	4.1	1.76	
	1/10	13.2	1.76	1.74
5.....	1/4	3.4	2.04	
	1/10	11.3	1.95	1.93
6.....	1/4	3.5	2.00	
	1/10	11.2	1.97	1.95
7.....	1/4	3.9	1.84	
	1/10	12.5	1.83	1.82
8.....	1/4	3.9	1.84	
	1/10	12.2	1.86	1.83
9.....	1/4	3.5	2.00	
	1/10	10.8	2.02	2.01
10.....	1/4	2.8	2.44	
	1/10	8.5	2.40	2.52 ¹
11.....	1/4	4.1	1.76	
	1/10	13.6	1.73	1.83 ¹
12.....	1/4	2.7	2.52	
	1/10	8.0	2.51	2.59 ¹
13.....	1/4	4.4	1.63	
	1/10	16.0	1.56	1.60

In the Turbidimetric Sulphur Table the figures obtained by readings less than 2.5 centimeters are to be regarded as only approximately correct. In such a case it is preferable to take a smaller proportion, bringing the reading between 2.5 cm. and 17.0 cm.

As a result of this investigation, the procedure in the case of the coal sulphurs has been modified at this laboratory, and is now conducted as follows:

After the combustion in the Mahler bomb the latter is rinsed with several portions of distilled water, amounting in all to about 150 cubic centimeters. This is filtered if necessary, and then titrated with N/10 sodium carbonate, using methyl orange as

¹ On standing for some time, some of the tablets become coated with a thin layer of effloresced salt. This should be removed by gently rubbing between the fingers before using the tablet. It is not advisable to keep the tablets in a moist atmosphere to prevent this efflorescence, as they become extremely hard and difficult to dissolve.

¹ Barium sulphate contaminated, apparently with iron.

indicator. The titrated solution is then made up to 200 cc. The amount of acidity found is used as a guide in selecting the aliquot for a sulphur determination. In the case of anthracite coals, the amount taken is one-fourth to one-half; in the case of soft coals from one-fourth to one-tenth of the whole. This portion is measured into the turbidimeter tube, diluted, mixed, and treated as described above. The precipitated solution is read at least twice, and the readings usually check exactly, unless they fall in the upper part of the tube, where they may differ by a centimeter without materially altering the results. In this case readings may be averaged. The amount of sulphur corresponding to the depth of liquid in the tube is found in the table, and multiplied by the proper factor, depending on the aliquot of the original solution taken. The average time required for these tests, including the cleaning of the vessels used, was found by the writer to be 10 minutes per test.

All dilutions must be made before precipitation, for otherwise the results will not be concordant for different dilutions.

PRACTICAL NOTES ON THE CANDLE TURBIDIMETER.

The flame should be protected from drafts, since it is almost impossible to obtain a good end point with a flickering flame. The wick should be kept trimmed so that the flame will be between 30 and 40 millimeters long, in order to prevent the deposition of soot on the bottom of the glass tube.

The glass tube should be kept clean. The barium sulphate adheres to the glass and cannot be rinsed out, but must be removed by means of a brush.

The readings should be taken in diffused daylight. The eye should be held quite near the top of the graduated tube, sighting in such a way that the image of the flame appears in the center of the bottom of the tube.

Since the 100 cc. mark on different tubes varies from 16.6 to 17.6 cm., if the sulphate solution contains less than 1.5 milligrams of sulphur in 100 cc., more than 100 cc. must be taken for the test in order to obtain enough of the turbid liquid to efface the image of the flame. The procedure is just the same as when 100 cc. or less are used, but the sulphur value found in the table is the amount contained in 100 cc. of the solution.

SUMMARY.

This investigation was made in order to determine the causes of observed variations between the gravimetric results of sulphate determinations and those obtained by means of Jackson's candle turbidimeter. It was found:

1. That variations in the size of the flame or of the distance between the top of the candle tube and the bottom of the glass tube made no appreciable difference in the results.
2. Nitrates in the solution, in quantities such as are found in coal analyses, do not affect the results.
3. A large excess of free hydrochloric acid tends to give low results in weak sulphate solutions. Aliquots of neutral solutions should not be acidified

until they are diluted nearly to 100 cc., since addition of all the acid to the undiluted portion was found to be followed by variable results.

4. The chief cause of the difference above referred to was found to be difference in the size and hardness of the barium chloride crystals used. The remedy found to be effective was the use of barium chloride in tablet form, whereby the weight and volume of the precipitant, as well as the texture of the precipitate, is rendered uniform in all tests.

5. By using the candle turbidimeter according to the method recommended in this paper, uniform and sufficiently accurate results may be obtained, and the method has been found very useful for making daily routine tests in large numbers. This applies to the determination of sulphur in coal, cement, and boiler waters. The sulphate in the latter may be determined without concentration if present in quantity of more than 37 parts per million of SO_4 . For amounts less than this the water must be concentrated by evaporation.

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THE ACCURATE TECHNICAL ESTIMATION OF THE CALORIFIC VALUE OF ANTHRACITE COAL.

By A. G. BLAKELEY AND E. M. CHANCE.

Received May 25, 1911.

Though much has been published upon the subject of fuel calorimetry in general, it is nevertheless true that but little has been written upon that phase of this subject dealing with anthracite coals. Moreover, the value of that which has been published is in a large measure discounted because the coals examined were not an example of the usual merchant sizes. Thus in the paper published by Parr and Wheeler¹ the two anthracites described contained but 11 per cent. and 13 per cent. of ash respectively. Palmenburg, on the other hand,² has published the results of an examination of a series of much more representative coals, which range from 9 to 27 per cent. ash, and which may be considered as covering practically the whole range of the merchant coals. It is frequently stated in the literature of this subject, that with high ash anthracites it is necessary to apply a correction for unburned carbon. Under the conditions which usually obtain, this statement is undoubtedly true, and while we may know that an error is ever present, the methods suggested for its correction are of but doubtful value. Such methods include the weighing by difference of the unburned carbon³ and the mixing of the coal to be burned with a smaller quantity of a substance of relatively high calorific value.

This second well-known method⁴ has recently been brought forward by Palmenburg as an original solution of this troublesome question. While this method will

¹ THIS JOURNAL, 1, 573.

² *Ibid.*, 2, 404.

³ Parr and Wheeler.

⁴ "Engineering Chemistry," T. B. Stillman, 4th Ed., 1910, pp. 131 and 139; "Fuel, Water and Gas Analysis," J. B. C. Kershaw, 1907, p. 49; "The Calorific Power of Fuels," H. Poole, 2nd Ed., 1907, p. 68.

doubtless give accurate and concordant results, it is only with the greatest care and skill on the part of the operator that such a desirable issue can be expected. The writers have found that with this method the bituminous coal underlying the anthracite is rapidly raised to a high temperature, and that the large volume of gases thus produced are likely to project small particles of the anthracite out of the nickel capsule and thus permit them to escape combustion. Thus, after a combustion it is no uncommon thing to find small particles of unburned coal lying upon the floor of the bomb. Another source of error worthy of attention is that a greater error is incurred in weighing a small quantity of a coal of high heating value than in weighing a large quantity of coal of low heating value, and that this whole error in weighing is calculated as error in the heating value of the anthracite. Thus the errors in weighing and sampling in both the anthracite and its kindler are concentrated as error in the heating value of the anthracite itself. Moreover, this error is multiplied $1\frac{1}{4}$ times as 0.8 gram of the anthracite is taken instead of 1 gram. Of course it is understood that these errors are generally small, but the writers hope to show that they are entirely avoidable.

A few determinations by the method of the addition of a kindler are appended compared with determinations by our routine method.

TABLE A.

Number.	Per cent.		Asbestos method.	
	Soft coal.	B. T. U.	B. T. U.	
C-2241.....	30.31	10440 ¹	
"	31.02	10690 ¹	10740	
"	32.68	10720 ¹	10770	
C-3022.....	31.37	9860 ¹	10010	
"	30.20	9920 ¹	10040	
C-2300 ²	14800	
"	14850	

A total of approximately 1 gram of the anthracite and kindler was used for each determination.

When first the Atwater calorimeter was applied to the determination of the calorific value of anthracites in this laboratory, the usual difficulties were encountered. Upon observation it was noted that while the upper or exposed surface of a high ash anthracite might be completely burned to ash, the lower stratum, or that part in immediate contact with the nickel capsule, would, in the vast majority of cases, be completely unconsumed. Thus it would seem that the real cause of the incomplete combustion was the chilling of the coal by the rapid conduction of heat through the nickel capsule and heavy platinum wire. The thermal insulation of the coal from the nickel capsule was then tried, with most satisfactory results. This insulation was brought about by lightly tamping into the bottom of the capsule a layer, about 3 mm. thick, of soft, previously ignited, asbestos. By this slight modification we have been enabled to burn completely and without difficulty coals containing as much as 40 per cent. of ash. The coal burns completely, leaving the ash either as a porous mass or a small

vitreous globule. In either case the residue is free from unburned carbon as is proved by its failure to lose weight when dried and then ignited.

Briefly the procedure is as follows:

A nickel capsule, 15 mm. in height by 25 mm. in width, is chosen, and a fair-sized pinch of soft, thoroughly ignited, asbestos is placed in it. This asbestos is then lightly tamped in place with some blunt instrument such as the butt end of a fountain pen. This mat of asbestos may be readily formed with the pen so as to present a concave depression with the center, perhaps 2 mm. lower than the edges. The mat at its thinnest point, its center, should be not less than 2 mm. thick. The coal, which should at least pass a screen of 80 meshes to the linear inch, after weighing in counterpoised scoop or bottle is then poured into the capsule, which is placed in the bomb, and the usual routine of combustion pursued, except that a pressure of oxygen of 25 atmospheres is used.

It will be seen at once how slight is this divergence from the usual routine. The increased accuracy to be gained is not so obvious. To test the accuracy of the determinations by this method we calculated from the determined calorific value of the coal the heating value per pound "unit coal," by the formula of Parr and Wheeler.¹

This scheme has been found admirably adapted to such a purpose, for though the heating value per pound unit coal of anthracites from different localities may vary widely that from the product of the same breaker will adhere more closely to a mean, an exception being the occasional intermixture of badly weathered coals with the usual freshly mined material. A few of these results may not be out of place as illustrative of these statements. It should be noted that these results are taken from the daily routine and are in no case the result of work performed with a view to future publication.

When reviewing such a table as the following the fact should be borne in mind that the formula by which the values were obtained is but an approximation having no absolute accuracy and that the errors

TABLE B.

C	Test No.	Colliery and information.	Per cent.					Heating value per lb. dry coal in B. T. U.	Heating value per lb. unit coal in B. T. U. (Parr and Wheeler).
			moisture.	volatile matter.	fixed carbon.	ash.	sulfur.		
H.	2521 ²	Gilberton boiler tests.	7.64	5.44	68.98	17.94	0.81	11950	15160
	2508 ²		9.96	3.34	60.37	26.33	0.83	10400	15320
	2365 ²		9.87	3.52	62.05	24.56	0.69	10760	15280
	3040 ²	Hammond boiler tests.	6.61	4.79	62.94	25.66	0.78	10640	15170
	3039 ²		7.78	4.32	64.23	23.67	0.71	11010	15270
	1760 ²		5.21	5.23	68.26	21.30	0.45	11400	15070
	1759 ²		5.99	5.28	65.73	23.00	0.54	11260	15190
	2099 ²	Wadesville.	9.27	5.38	71.21	14.14	0.65	12390	14920
	2153 ²		10.49	4.94	66.11	18.46	0.65	11600	14950
	1291 ²	Boston Run tests.	4.61	4.41	60.29	30.69	0.80	9720	14940
	1220 ²		9.20	2.94	58.00	29.86	1.26	9510	14830

¹ Bull. 37, University of Illinois, Engineering Experiment Station.

² As these coals were fired wet, the samples were preserved in air-tight containers, the moisture being determined prior to grinding.

¹ Poor burn.

² Soft coal used as kindler.

TABLE B (Continued) —VEIN SAMPLES.

Test No.	Lift.	Per cent. moisture.	Per cent. volatile matter.	Per cent fixed carbon.	Per cent ash.	Per cent sulfur.	Heating value per lb. dry coal in B. T. U.	Heating value per lb. unit coal in B. T. U. (Parr and Wheeler).
C 2381	E 5th	2.82	5.85	87.88	3.45	0.56	15100	15680
2382	6th	2.06	6.92	85.20	5.82	0.59	14530	15550
2388	W 8th	1.39	7.27	83.06	8.28	0.59	14040	15410
2637	W 5th	2.50	6.47	73.27	17.76	0.52	12570	15670
2638	E 5th	2.06	7.46	78.88	11.60	0.52	13620	15630
2639	W 4th	2.80	6.93	74.06	16.21	0.34	12880	15720
2640	W 6th	2.45	6.44	80.95	10.16	0.50	13860	15630
2641	W 3rd	1.94	7.85	50.17	40.04	0.35	8650	15490
2642	W 1st	1.81	7.35	69.37	21.47	0.40	11960	15670

TABLE B (Continued).

Test No.	Size of coal.	Per cent. moisture.	Per cent volatile matter.	Per cent. fixed carbon.	Per cent ash.	Per cent sulfur.	Heating value per lb. dry coal in B. T. U.	Heating value per lb. unit coal in B. T. U. (Parr and Wheeler).
C 2572	Stove.....	1.70	6.45	79.33	12.52	0.57	13410	15560
C 2573	Chestnut	2.10	6.38	76.14	15.38	0.54	12830	15470
C 2574	Pea.....	2.51	7.20	71.14	19.15	0.56	12230	15540
C 2575	Buckwheat .	1.39	6.45	73.86	18.30	0.58	12490	15640
C 2576	Rice.....	2.13	6.69	71.40	19.78	0.57	12290	15750
C 2577	Barley.....	2.44	6.90	69.80	20.86	0.50	12120	15780
C 2776	Broken.....	2.95	5.57	80.75	10.73	0.55	13660	15530
C 2777	Flat jig stove	2.66	6.40	74.27	16.67	0.56	12670	15570
C 2778	Stove.....	2.65	6.12	78.35	12.88	0.53	13290	15520
C 2779	Chestnut ...	3.04	5.84	77.67	13.45	0.56	13250	15640
C 2780	Pea.....	2.92	6.42	72.60	18.06	0.54	12440	15590
C 2781	Buckwheat .	2.89	6.64	72.60	17.87	0.54	12490	15610
C 2782	Rice.....	2.92	5.92	74.52	16.64	0.52	12690	15600
C 2783	Barley.....	2.68	6.46	74.59	16.27	0.55	12750	15580
2792	Stove.....	2.25	8.09	78.73	10.93	0.54	13760	15670
2793	Chestnut....	2.12	6.78	78.18	12.92	0.51	13350	15590
2794	Pea.....	1.86	6.67	71.66	19.81	0.50	12230	15670
2795	Buckwheat	0.66	6.25	75.58	17.51	0.46	12640	15630
2796	Rice.....	1.96	7.07	71.30	19.67	0.49	12160	15550
2797	Barley.....	2.28	6.77	75.21	15.74	0.47	12810	15530

of the proximate analysis as well as those of the actual calorimetric determination are reflected in the heating value per pound unit coal.

For the sake of comparison the values published by Palmenburg (*Loc. cit.*, p. 406) have been calculated to heating values per pound unit coal, by the formula of Parr and Wheeler. The values published have been assumed to have been determined on, or calculated to, the dry coal.

TABLE C.

No.	Per cent. Ash.	Heating value per lb. unit coal (Parr and Wheeler).	Determination from which taken.
328	26.58	14790	second
330	20.19	14970	first
330	20.19	15080	second
330	20.19	15030	mean
333	14.36	14790	mean
438	14.29	14840	mean
440	25.20	14990	mean
442	20.26	14890	mean
444	23.62	14900	mean
462	15.22	15010	mean
399	21.23	14880	mean
400	21.67	14940	mean
494	8.99	15130	mean

It may be well to note that the above results were obtained with the Atwater calorimeter, the water equivalent of which was determined by burning samples of naphthalene and hippuric acid as recommended by Atwater in his original article.¹

Although having no direct bearing on the method, it may be of interest to state here that this particular Atwater calorimeter has been slightly modified by us for convenience in manipulation. The screw cap socketed for a spanner on the original apparatus, has been replaced by a screw cap bearing a hexagon head. Thus by substituting a box wrench for the original spanner, the annoying tendency to slip has been removed. The stirring motor together with an upright some 42 cm. high have been mounted upon a piece of oak board, free to move upon the calorimeter table. This upright supports a walking beam, one end of which is connected by a driving rod direct to the crank of the motor, while the other end of the beam may be thrust into the ring of the stirrer, thus giving the stirrer a positive movement much to be preferred to the more or less uncertain motion imparted to it by the usual string and pulley device.

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PREPARATION OF NEUTRAL AMMONIUM CITRATE SOLUTIONS BY THE CONDUCTIVITY METHOD.

By ROBERT A. HALL.
Received May 8, 1911

In their investigations of the proportions of aqueous solutions containing ammonia and citric acid,² Hall and Bell found that the neutral point of the solution could be detected by conductivity measurements, and this suggested the application of the conductivity method as a possible means of preparing the neutral ammonium citrate solution required in fertilizer analysis for the determination of the citrate-insoluble phosphoric acid in a fertilizer. In order to ascertain the possibility of readily and easily preparing neutral ammonium citrate by the application of the conductivity method the following experiments were made by the author of this article.

A citric acid solution was prepared of such a citrate content that when neutralized by ammonia its specific gravity would be greater than 1.09 at 20°; that is, 370 grams of pure citric acid³ were dissolved in ammonium hydroxide of 0.90 sp. gr. and water, until the solution was near the point of neutrality, yet leaving the solution acid to litmus paper. Care was taken that the volume was not over one liter. The solution was allowed to stand over night to cool. It was again tested with litmus paper to see that it was distinctly acid. Also, small portions, one to two cc., were withdrawn with pipettes and roughly titrated with a diluted ammonia solution in order to ascertain the approximate amounts of ammonia solution necessary to make the citrate solution distinctly alkaline to litmus. The diluted ammonia solution used was prepared by taking the concentrated am-

¹ *J. Am. Chem. Soc.*, **25**, 659.
² *Ibid.*, **33**, 711.
³ Method of Analysis, *Bull.* **107**, Bureau of Chemistry, p. 1.

monium hydroxide, sp. gr. 0.90, and diluting exactly ten times, that is, 100 cc. were diluted to one liter. A sufficient amount of this solution was prepared to have enough for the making of the solution for the conductivity measurements and also for addition to the larger bulk of the acid ammonium citrate solution,

of the calculated amount, as shown by the conductivity measurements, for complete neutrality. 100-cc. lots of the nearly neutralized ammonium citrate solution were withdrawn with pipettes and put in 200 cc. volumetric flasks. Definite amounts of the diluted ammonia solution were measured into these differ-

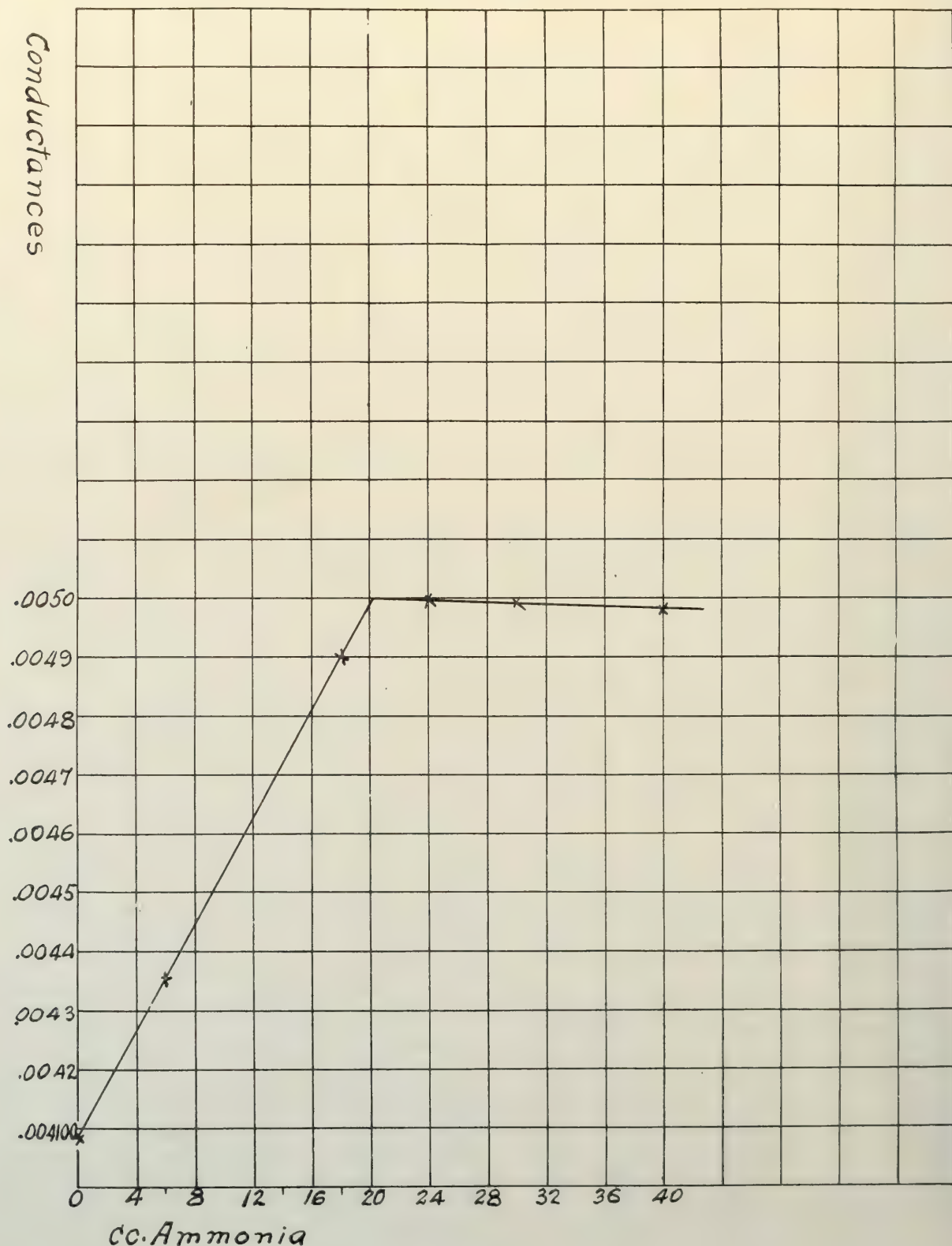


Fig. 1.

ent flasks. Water was then added to the mark, the solution thoroughly mixed, and the flasks placed in an electrically controlled thermostat. The temperature of this thermostat was maintained at 25° , plus or minus 0.01° . When these solutions had come to the temperature of the bath their conductivities were determined with a Wheatstone bridge in the usual way. The conductivity cell used was the H. C. Jones type for concentrated solutions. The conductances were plotted against the cc. of the ammonia solution used. It was easy to read from the curve thus obtained the number of cc. of the ammonia solution needed to neutralize exactly 100 cc. of the acid ammonium citrate solution used. This amount of the diluted ammonia solution was then measured into a 200 cc. flask containing 100 cc. of the citrate solution and water added to the mark. After thorough mixing, the flask was placed in the bath and allowed to come to bath temperature. Its conductivity was then ascertained. Its conductance showed it to have the amount of ammonia necessary for exact neutralization. The solution, when tested with corallin, methyl orange, methyl red, and neutral litmus paper (Squibb's), gave no evidence of the presence of excess of either acid or base. Also, the solution was shaken out with chloroform, the chloroform separated from the citrate solution and shaken with water and the water tested for ammonia.¹ No ammonia was found. Hence it was concluded that a neutral ammonium citrate solution had been prepared with accuracy and certainty.

Specific gravity determinations were also made of the solution used in these conductivity determinations and the densities plotted against the cc. of ammonia. The curve showed that the neutral solution as prepared by the conductivity had the highest specific gravity.¹

In Table I is given the data obtained in these measurements, and in Fig. 1 the conductances are plotted against the cc. of ammonia solution used:

TABLE I.

Solution No.	Cc. ammonia.	Conductivity.
1.....	0.00	0.004085
2.....	6.00	0.004353
3.....	18.00	0.004900
4.....	24.00	0.004997
5.....	30.00	0.004991
6.....	40.00	0.004980
7.....	20.30	0.004999

The neutral solution as prepared above had a specific gravity greater than 1.09 at 20° . It was therefore an easy matter to dilute with distilled water and in the usual way bring to the required density.

In order to investigate the possibility of the use of the conductivity method of preparing neutral ammonium citrate solution by the chemist who has not the use of an electrically controlled thermostat, or a thermostat regulated by any other method wherein a constant temperature is secured, a series of experiments were made in which the use of the regulated thermostat was dispensed with; that is, the elec-

trical control was cut off and the temperature of the bath was allowed to vary with that of the room. However, a time for experimentation was chosen so that there was a minimum of variation of room temperature. In brief, the experiments were conducted under such conditions as can be had in any laboratory where a room fairly well protected from the usual weather variations and from the presence of those entering and leaving the room during the time of the experiment can be had. In the place of the thermostat a tub of water could have been used for the bath.

The solutions were prepared as above, placed in the bath and allowed to come to the temperature of the bath. Erlenmeyer flasks of suitable volume and of such sized mouth as to admit of easy entrance of the electrodes of the cell were placed in the bath, so that when the solutions were being changed in the cells the electrodes could be placed in these flasks and be kept at the temperature of the bath, thus preventing the slight lowering of temperature due to the evaporation of the water on the electrodes. The conductivity measurements were made as rapidly as possible (each series was run in less than one and one-half hours), the cells and electrodes being carefully washed each time with the new solution. This rinsing was repeated three times for each change of solutions. During the short intervals of waiting necessary for the cell and its solution to come to bath temperature again after the handling the conductances were computed and the curve plotted, so that as soon as possible after the last reading was made the last point in the curve was located and the curve completed. It was found further that by plotting the bridge readings against the cc. of ammonia solution used that the same results were obtained as by plotting the conductances against the cc. of ammonia solution. In this way it was possible to make the series of six measurements in a very short time, usually less than one and one-half hours being required, and thus minimize the probability of any great change of room temperature. From the curve was read the amount of ammonia solution needed to be added to 100 cc. of the acid ammonium citrate in order exactly to neutralize it. This amount of ammonia was run into a 200 cc. flask containing the solution previously measured out, water added to the mark, and the solution thoroughly mixed. The flask was then placed in the bath and brought to the temperature of the bath. The conductivity measurement was then made. It was found that the bridge reading obtained corresponded exactly to the bridge reading on the curve for neutral ammonium citrate solution. The same amount of ammonia was then run into another 100 cc. lot of the ammonium citrate solution and this solution made up to a specific gravity of 1.09 at 20° . When these solutions were tested with indicators and chloroform, as above, they gave no evidence of containing either acid or free ammonia in excess.

The bath was now brought again to a temperature of 25° and maintained there by the electrical control

¹ Hall and Bell, *Loc. cit.*

while the conductivity measurements were repeated. These gave a curve showing the neutral point to be the same as that found at room temperature.

In Table II are given the data of the measurements made at room temperature. In Fig. 2 the bridge-readings are plotted against the cc. of ammonia solution used:

TABLE II.

Solution No.	Cc. ammonia.	Bridge-reading.
1.....	0.00	49.40
2.....	10.00	52.01
3.....	18.00	54.09
4.....	24.00	54.80
5.....	30.00	54.75
6.....	36.00	54.70
7.....	20.80	54.84

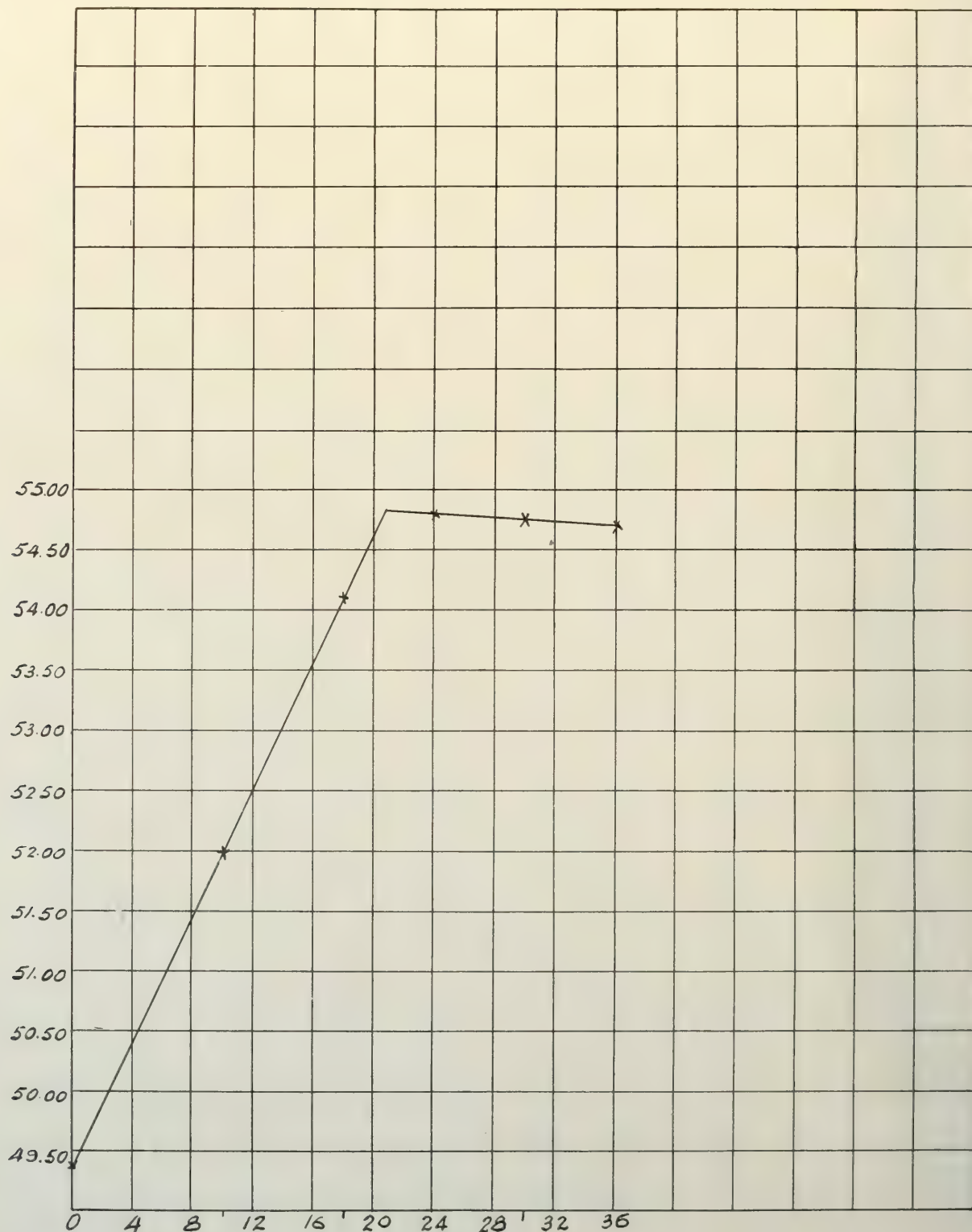


Fig. 2.

An effort was made to ascertain the possibility of preparing a neutral citrate solution by adding an excess of ammonia and afterwards removing this excess by extractions with chloroform.¹ Although repeated extractions were made, there was always free ammonia remaining in the citrate solution. This was to be expected, as the ammonia is so much more soluble in water than in the chloroform. Moreover, had it been possible to extract all the free ammonia from the solution the chloroform that would have remained in solution in the citrate solution would have precluded the use of this method for the preparation of neutral ammonium citrate for the fertilizer analysis, as the chloroform would be decomposed, forming free hydrochloric acid, which would interfere with the determination of the citrate insoluble phosphoric acid.

CONCLUSION.

It has been shown that the conductivity method of preparing neutral solutions is applicable to the preparation of exactly neutral ammonium citrate solutions of such a density that they can, after neutralization, be diluted with distilled water and brought to a density of 1.09 at 20°. This method can be applied under conditions such as can easily be obtained in any laboratory and therefore seems worthy of adoption as an "Official Method" of preparing the exactly neutral ammonium solution required in fertilizer analysis for the determination of the citrate insoluble phosphoric acid content of the fertilizer. For the regulated thermostat there may be substituted a tub of water. However, a thermostat of constant temperature is preferable, for then there is no necessity of the measurements being carried out so quickly as when the measurements are made in a bath at room temperature.

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A POLARISCOPIC METHOD FOR THE DETERMINATION OF MALIC ACID AND ITS APPLICATION IN CANE AND MAPLE PRODUCTS.

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In the following report there is developed, from extensive original data, a polariscopic method for the estimation of active malic acid which is applicable to a wide range of mixtures without previous isolation or purification of the malic acid. Methods are also developed for a partial separation of malic acid which makes the method of estimating it applicable to an additional wide range of natural products and artificial mixtures. Some applications of the method in the examination of cane and maple syrups are reported. Supplemental to this are notes on a method for tartaric acid, less fully worked out, and a plan for applying these methods to determine both these acids in a mixture of the two, without previous separation of them. This was

¹ Hall and Bell, *Loc. cit.*

² This paper is an abridgment of a paper by the author on the same subject presented at the 42nd general meeting of the American Chemical Society, July 12, 1910.

worked out incidental to an investigation on the acid constituents in sugar cane.

The methods described in the literature for determining the organic plant acids are in many particulars far from satisfactory, even when applied to fruit juices or fermentation products, for which most of them were worked out. In sugar cane juice and its products, new difficulties are encountered. With perhaps none of the commonly occurring organic plant acids have the methods hitherto in use¹ proved more unsatisfactory than with malic acid. In the cane juice, besides the inconvenience occasioned by the large amount of sugar present, the aconitic acid, which is a prominent constituent, introduces special difficulties in that its salts with such bases as are usually available for the separation of organic acids are not widely different from those of malic acid. Therefore a method for its determination which is at once accurate and applicable to a wide range of mixtures will doubtless be welcomed by the many analysts who have occasion to deal with products containing it, such as maple products, fruit juices, fermentation products, etc., as well as by investigators who seek to ascertain for the first time its occurrence or non-occurrence in various substances.

Among analytical operations described in the literature referring to malic acid are several processes, depending upon group reagents, yielding results that are arbitrarily reported as malic acid or more properly as "malic acid values," without presuming in them any ultimate determination of malic acid. Thus a convention has been in vogue in cider and vinegar analysis of computing and reporting the total non-volatile acids, or organic acids, as malic acid.²

In the older text-books the method of R. Kayser³ was commonly given for malic acid in wines. This method is based upon the assumption, that the malate is the only soluble salt of a non-volatile organic acid that barium chloride forms in wine in the presence of sodium carbonate and freed from alcohol. This is true, however, only of a relatively narrow class of natural products. Succinic, citric and aconitic acids besides others all form water-soluble salts with barium, hence in their presence this method could not be applied.

A method somewhat similar to the last but with calcium substituted for the barium, as proposed by Leach⁴ for wine and vinegar analysis, has similar limits to its range of usefulness.

In the examination of maple products and suspected adulterations and imitations of maple products it is usual to determine the amount of calcium precipitated by the neutral solution in the presence of alco-

¹ Schmidt and Hepe, *Z. anal. Chem.*, **21**, 534-541 (1882); *Bull.* **107**, (revised), Bureau of Chem., U. S. Dept. of Agr., p. 80; G. Joergensen, *Z. Unters. Nahr. Genussm.*, **13**, 241 (1906); **17**, 396-412 (1909); *Chem. Abs.*, **1**, 1448 (1907); **3**, 1781 (1909); F. Mutellet, *Annales des Falsifications*, **2**, 383-6. Some notes on such means of separating organic acids and on estimating others of them than malic acid forms the subject of a separate paper.

² Allen's "Commercial Organic Analysis," 4th Ed., **1**, 187, 505.

³ *Ibid.*, 3rd Ed., **1**, 512; König's *Untersuchungsmethoden an gewerblichen wichtiger Stoffe*, 2nd Ed., p. 588. (The newer editions of both these works omit Kayser's method for malic acid.)

⁴ Leach's "Food Inspection and Analysis," 2nd Ed., **1909**, pp. 702, 768.

hol to the extent of 75 or 85 per cent.¹ The alkalinity of the ash from this precipitate, computed as per cent. malic acid, gives the so-called "malic acid value." This is a very convenient operation and at present serves a very useful purpose when it is merely a question of distinguishing between pure maple products and those adulterated by the addition of relatively pure cane sugar or glucose. If, however, it is a question of detecting in maple products the addition of substances having impurities such as occur in cane molasses or syrup, it has little value, as will be shown further on in this report.

The results from a determination of a "lead number" by precipitation with lead subacetate, as in the methods for maple products according to Hortvet,² Winton,³ or Winton and Ross,⁴ can also have a close relation to the amount of malic acid present only in those exceptional cases in which there is present no considerable amount of other precipitate-forming organic or inorganic acid, as in maple sugar products and these mixed with pure sugars.

It is a common experience with optically active substances that slight changes in their composition or in the combination into which they have entered are accompanied by changes in their rotatory power. Thus salts of active acids or bases, alcoholates and esters of active alcohols, etc., we would expect to have different rotatory powers from those of the free compounds although the elements or groups entering into combination with them may not be active. A place among such combinations very exceptional in the extent of this change in the rotatory power is taken by the compounds formed by certain active dicarboxylic oxy-acids with a few of the rarer elements, especially with molybdenum, tungsten and uranium, in that the activity is increased many fold. Thus P. Walden,⁵ who was the first to discover that this property belonged also to uranium, reported that it increased the levo-rotatory power of malic acid over 500-fold and that of tartaric acid 20-fold. A. F. Holleman⁶ studied the effect of uranyl nitrate on saccharic acid. H. Itzig⁷ studied the compounds of uranium with tartaric and malic acids, seeking primarily to determine the constitution of these uranium compounds. Rimbach and Schneider⁸ further studied the molybdenum and uranium compounds of quinic acid. H. Grossmann⁹ furnishes us with more details concerning the effect of uranyl compounds on some of these oxyacids and also made an extensive study of their effect on the rotatory power of a number of sugars. While this remarkable property of the uranyl compounds with the dicarboxylic oxyacids at once suggests the possibility of basing upon this property quantitative methods for the estimation and identification of individual

members of the group of acids, no such method has yet been published as far as I have been able to find. Seeking to elaborate such a quantitative method which should enable me to make reasonably quick and accurate estimations of malic acid in the sugar-cane products, I carried out many series of tests to answer the questions suggested by the sub-headings which follow under the heading "Experimental Basis." Some of these were apparently answered in advance by the data of the investigators cited above, but as my results were in part contradictory to those given by the above, and were in part obtained under different conditions, I shall here give the conclusions based upon my own experimental data. Space does not permit presenting here all the rather extensive tables of the data involved.

In the collection of these data, the polarizations were made with a Schmidt and Haensch quartz wedge, double compensation instrument with readings on the sugar scale. As the limit of accuracy with clear solutions was 0.05 to 0.1 unit on the Ventzke scale, and somewhat more with solutions deeply colored yellow or brown from the uranium compounds, a corresponding latitude must be allowed in the conclusions.

I. EXPERIMENTAL BASIS FOR THE METHOD.

1. *The Maximum Effect.*—Under various conditions, approximately the same increase was occasioned in the levo-rotatory activity of the malic acid. In the most accurate determinations made of the rotation of the uranium-malic acid compound, using a "Kahlbaum" preparation of the acid, it was found that at 20° C. a 1 per cent.¹ malic acid solution, converted to the uranium compound, has a levo-rotation of 29.7 units on the Ventzke sugar scale, if white light from a Welsbach gas light is used, and 28.9 units when yellow, sodium light is used. From this we have for white light

$$[\alpha]^{20} = -515$$

and for yellow sodium light,

$$[\alpha]_{\text{D}}^{20} = -501.$$

The free malic acid, *i. e.*, without the addition of a uranyl compound, has a rotatory power so low that in a concentration like those used with the uranyl compounds, *viz.*, not much above 0.1 normal, the delicacy of the polariscope used did not suffice for very accurate determinations. With a 3.043 per cent. solution, the rotatory power was found equivalent to approximately 0.13 on the Ventzke scale computed for a 1 per cent. solution, or

$$[\alpha] = -2.25.$$

Comparing this number with -515 above, we find that the uranium causes a 229-fold increase in the rotatory power.²

¹ For brevity's sake the term "per cent." is used here and in what follows to mean grams per 100 cc.

² Walden (*Ber. d. chem. Ges.*, **30**, 2889-90 (1897)) reports $[\alpha]_{\text{D}}$ for malic acid equal to about -0.77 and $[\alpha]_{\text{D}}$ for malic acid with uranium added equal to -475. The latter number does not vary greatly from the corresponding result from my data, *viz.*, -501. From Schneider's formula for malic acid (Landolt's, *Das optische Drehungs-Vermögen*, 2nd Ed., p. 178. $[\alpha]_{\text{D}}^{20} = 5.89 - 0.0896q$), the specific rotatory power of a 1 per cent. solution is -2.98. Necessarily with such a low activity, the results of different experimenters must vary greatly.

¹ *J. Am. Chem. Soc.*, **30**, 1285 (1908); Official and Provisional Methods of Analysis, *Bull.* **107** (revised), Bureau of Chem., U. S. Dept. of Agr. p. 74.

² *J. Am. Chem. Soc.*, **26**, 1523 (1904); *Bull.* **107** (revised), Bureau of Chem., U. S. Dept. of Agr., p. 73.

³ *J. Am. Chem. Soc.*, **28**, 1204 (1906).

⁴ *Circular* **53** (1910), Bureau of Chem., U. S. Dept. of Agr.

⁵ *Ber. d. chem. Ges.*, **30**, 2889 (1897).

⁶ *Rec. des travaux chimiques des Pays-Bas et de la Belgique*, **326**, 189.

⁷ *Ber. d. chem. Ges.*, **34**, 3822 (1901).

⁸ *Z. physik. Chem.*, **44**, 467 (1903).

⁹ *Z. d. Ver. deutsch. Zuckerind.*, **55**, II, 650, 941, 1058 (1905).

2. *Influence of Concentration of the Malic Acid.*—In a series of tests with various concentrations up to 1.3 per cent., it was seen that with a plentiful supply of the uranium compounds, *i. e.*, with 1.25 or more atoms of U to each molecule of malic acid, the variation in specific rotatory power due to the concentration of malic acid, if there be any variation, is within the limits of the experimental error in these tests. With a scant supply of uranium, *e. g.*, 1.04 atoms, the results are all too low, but there is a tendency towards higher results with more dilute solutions.

3. *Influence of Kind of Uranyl Compounds Used.*—Provided it is soluble and capable of reacting with the malic acid and no interfering by-product is formed, the kind of uranyl compound used has little or no influence. Uranyl acetate and sodium and potassium uranates were used. In using the uranates (prepared from the acetate or nitrate by precipitation with sodium or potassium hydroxide and incomplete washing) the alkalinity imparted by these salts had to be neutralized to get the maximum effects. The uranyl nitrate, used alone with malic acid, is unsuited because the

by-product, nitric acid, interferes, as will be shown under "Interference of Foreign Substances." For convenience of application and for a wide range of conditions giving the maximum effects, uranyl acetate is preferred. Commercial preparations of sodium uranate and of uranic acid were found unsuited for the reaction. The uranyl acetate used in most of the work contained 51.56 per cent. uranium (theoretical for $(\text{UO}_2)(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{aq.}$, 56.04 per cent.). It did not completely dissolve in weak acids like malic acid, necessitating filtering before polarizing. By recrystallizing from a hot filtered solution, and drying the crystals at a temperature not above 50°, I succeeded in preparing crystals which dissolved completely.

4. *Influence of the Quantity of the Uranyl Compound.*—The proportion of 1 atom U to 1 molecule of malic acid, which we may presume is the theoretical amount required, will not suffice to call forth the maximum rotation. Using successively larger amounts, the action increases gradually until about 1.25 atoms U to 1 molecule malic acid is reached, after which it remains constant. Presumably, by the law of mass

TABLE I.

Effect of other acids and of alkali upon the rotatory power of the malic-acid-uranium compound. In each case, unless otherwise stated, the concentration of the malic acid was 0.1 N. Polarizations are computed on a 1 per cent. solution.

The uranium was added as uranyl acetate and, unless otherwise stated, in the proportion of 1.25 atoms U to each molecule malic acid. The acidity numbers refer to standards in Table III of shades of methyl orange, depending upon the concentration of H ions.

No. of line.	Other acids added. cc. normal acid to 15 cc.	Cc. normal KOH added to 15 cc.										
		0	1.0	1.5	2.0	2.5	3.0	4.0	4.5	5.0	6.0	7.5
1	None.....	Acidity	2	11	14	14
		Polarization	29.28	28.26	27.45	27.99
2	3 cc. acetic.....	Acidity	2	11	...	13	13	14	14	...
		Polarization	29.24	29.06	...	28.36	27.75	26.63	25.93	25.29
3	6 cc. acetic.....	Acidity	4-5	7	...	11	...	12
		Polarization	27.05	...	29.08	28.58	...	28.47	...	27.84
4	3 cc. formic.....	Acidity	1-2	2-3	...	3-4	4-5	6	11	...	13	14
		Polarization	26.11	28.72	...	28.82	29.00	29.45	28.79	...	26.66	24.74
5	3 cc. lactic.....	Acidity	1-2	2-3	...	3-4	4-5	6-7
		Polarization	21.16	27.26	...	28.26	28.29	28.29
6	3 cc. succinic.....	Acidity	2	2-3	...	7	9	11
		Polarization	27.76	27.91
7	3 cc. citric.....	Acidity	2	...	4	11	...	13-14
		Polarization	10.47	...	16.54	19.40
8	3 cc. citric (1).....	Acidity
		Polarization	26.14
9	3 cc. citric (2).....	Acidity
		Polarization	23.24	...	30.19	29.23	...	27.60
10	3 cc. citric (3).....	Acidity
		Polarization	30.30
11	3 cc. aconitic.....	Acidity
		Polarization	25.26	29.15
12	3 cc. mucic.....	Acidity
		Polarization	27.90
13	3 cc. acetic and 3 cc. lactic.....	Acidity	1-2	2-3	5	...	7-8	...	11-12
		Polarization	21.30	26.72	27.26	...	26.69	...	27.91
14	3 cc. acetic and 3 cc. lactic (2).....	Acidity	...	25.74	27.34	...	27.57	...	27.14
		Polarization	26.71	28.22	28.76	...	28.32	...	27.89
15	3 cc. sulphuric.....	Acidity	1	1	1	2	11	14
		Polarization	1.37	24.56	...	28.49	28.35	27.69
16	3 cc. hydrochloric.....	Acidity	28.39
		Polarization
17	3 cc. nitric.....	Acidity	1	1	1	2	10-11	14
		Polarization	0.78	21.87	...	29.03	28.44	27.57
18	3 cc. sulphuric and 3 cc. acetic.....	Acidity
		Polarization	0.34	28.09
19	3 cc. hydrochloric and 3 cc. acetic.....	Acidity	1	...	1-2	4	...	7	11
		Polarization	0.48	21.26	...	27.94	28.26	...	28.12	28.02
20	3 cc. nitric and 3 cc. acetic.....	Acidity
		Polarization	0.32	19.93	...	27.94	29.39	...	28.48	28.39
21	3 cc. nitric and 3 cc. acetic.....	Acidity	1-2
		Polarization	0.75	28.00

(1), (2) and (3)—The amount of uranium acetate in these is increased to 1.67 atoms in (1), 2.1 atoms in (2) and 2.5 atoms in (3) of U to one molecule of malic acid.

action, an excess of the uranyl compound is required to drive the reaction to completion.

5. *Interference of Foreign Substances.*—It is evident from the foregoing that with pure solutions of malic acid we can use the increased rotatory power imparted by uranyl compounds for quantitatively determining the amount with a degree of accuracy limited practically only by the accuracy of the volumetric measuring apparatus. But our difficulty has been to get the malic acid in a pure state without loss. We wish a method of estimating it after only a partial purification, such as we can readily effect. To determine to what extent such accompanying substances like small amounts of sugars or of bases and other acids interfere I carried out many series of tests from which some characteristic ones pertaining to acids and alkalies are collected in Table I.

(a) *Acids and Alkalies.*—From Table I, the following results are to be noted:

With no foreign acid added, the base, potassium hydroxide, interferes but little until enough is added to neutralize the malic acid (line 1).

The addition of two equivalents of acetic acid does not interfere nor is there any marked interference with the same partly or wholly neutralized, *i. e.*, with the addition of potassium acetate (line 2).

Four equivalents of acetic acid are sufficient to interfere perceptibly, but by partly neutralizing this, the maximum effect is again secured, which is but slightly reduced upon complete neutralization of the acetic acid added or its equivalent of malic acid (line 3).

In the cases of added formic or lactic acid, there is also a considerable range in the degree of neutralization through which it does not interfere seriously (lines 4 and 5).

The few trials made with succinic, aconitic and mucic acids leave it probable that with more tests a similar range of non-interference might be found.

The presence of two equivalents of the strong mineral acids almost completely destroys the effect of uranyl acetate. When these are neutralized, however, *i. e.*, when neutral salts are added, there is again little or no interference.

In another series of tests, not included in this table, in which sodium uranate was the reagent in place of uranyl acetate, the results ran similar except that, as may be expected, the sodium uranate exercises its neutralizing effect, as does the addition of its equivalent of potassium hydroxide.

Table II presents the results of a series of tests to determine the effect of larger amounts of potassium acetate and also the effects of the presence of the acetates of barium and calcium with and without an excess of acetic acid. Assuming no notable effect upon the rotatory power of the uranium-malic-acid compound by dilution, these tests with different amounts of added substances were made, for convenience, by additions of small measured volumes of strong solutions to definite volumes filled into the dry polariscope tube. For these additions a polariscope tube with tubulature and

TABLE II.

Further data on the effects of potassium acetate and acetic acid, and data on the effects of calcium and barium acetates and acetic acid upon the rotatory power of the malic-acid-uranyl compound.

No. of test, composition of original mixture, and temperature of tests.	Additions.		Polariscope readings.		Percentage which the rotatory power is of that of same concentration without additions.
	2 \times N acetic acid.	2 \times N KOH.	Actual.	Equivalent computed on original concentration and temperature.	
No. 348.—8 cc. malic acid sol. A + 0.8832 gram uranylacetate made up to 20 cc. tested at 30° C.	0	0	18.87
	3	0	16.70	19.20	101.6
	3	0.5	16.32	19.17	101.5
	3	1.0	15.94	19.13	100.7
	3	1.5	15.46	18.94	100.3
	3	2.0	15.06	18.82	99.6
	3	2.5	14.53	18.52	98.0
	3	3.0	14.16	18.41	97.5
	11.2	3.0	10.25	17.51	92.7
	11.2	4.3	9.85	17.48	92.5
	11.2	5.6	9.56	17.58	93.1
	11.2	6.9	9.12	17.37	92.0
	11.2	8.2	8.79	17.31	91.6
	11.2	9.5	8.45	17.19	91.0
	11.2	10.8	8.28	17.38	92.0
No. 374.—0.09 gm. moist malic acid crystals + 0.6 gram uranyl acetate made up to 15 cc. Tested at 30° C.	0	0	15.42
	3	0	13.10	15.72	102.9
	3	0.5	12.49	15.40	99.9
	3	1.0	12.04	15.25	98.9
	6	1.0	10.21	14.97	97.1
	6	1.5	10.08	15.12	98.1
	6	2.0	9.61	14.74	95.6
	9	2.0	8.28	14.35	93.1
	9	2.5	8.06	14.24	92.3
	9	3.0	7.91	14.24	92.3
	9	3.5	7.73	14.17	91.9
	9	4.0	7.60	14.19	92.0
	9	5.0	7.33	14.17	91.9
	9	6.0	7.25	14.50	94.0
	9	9.0	6.34	13.95	90.5
No. 375.—4 cc. of malic acid sol. B + 0.56 gram uranyl acetate made up to 12 cc. Tested at 26° C.	20% sol. barium acetate.				
	0	0	23.02
	0	2	18.51	21.59	93.8
No. 376 4 cc. of malic acid sol. B + 0.56 gram uranyl acetate + 1.6 cc. 20% barium acetate sol. made up to 12 cc. Tested at 26° C.	0	1.6	22.32	22.32	97.0
	0.5	1.6	21.37	22.26	96.7
	0.5	3.6	18.32	22.13	96.1
No. 377.—4 cc. of malic acid sol. B + 0.84 gram uranyl acetate + 1.6 cc. 20% barium acetate sol. made up to 12 cc. Tested at 27° C.	0	1.6	21.61	21.63	94.0
	0.5	1.6	20.96	21.85	94.0
	1.0	1.6	20.20	21.90	95.0
	1.5	1.6	19.51	21.97	95.0
	2.0	1.6	18.87	22.04	95.0
	2.5	1.6	18.04	21.82	94.0
	3.0	1.6	17.39	21.76	94.0
No. 378.—4 cc. of malic acid sol. B + 0.56 gram uranyl acetate + 1.6 cc. 10% calcium acetate sol. made up to 12 cc. Tested at 26° C.	10% calcium acetate.				
	0	1.6	22.81	22.81	99.0
	0.5	1.6	22.00	22.92	99.0
	1.0	1.6	21.05	22.80	99.0
	1.5	1.6	20.26	22.79	99.0
	2.0	1.6	19.50	22.75	98.0
	2.0	3.6	16.33	21.77	94.0
	3.0	3.6	15.10	21.39	92.0

No. 379.—4 cc. of malic acid sol. B + 0.84 gram uranyl acetate + 1.6 cc. 10% calcium ace- tate sol. made up to 12 cc. Tested at 24.5° C.	0	1.6	22.73	22.72	98.7
	0.5	1.6	21.92	22.80	99.0
	1.0	1.6	21.13	22.86	99.3
	1.5	1.6	20.42	22.94	99.7
	2.0	1.6	19.72	22.98	99.8
	2.5	1.6	19.06	23.00	99.9
	3.0	1.6	18.22	22.74	98.8
	4.0	1.6	17.02	22.66	98.4
	4.0	3.6	14.72	22.05	95.8
	5.0	3.6	13.65	21.59	93.7

with a bulb-tube set upon the tubulature (see Fig. 1) was found very convenient.

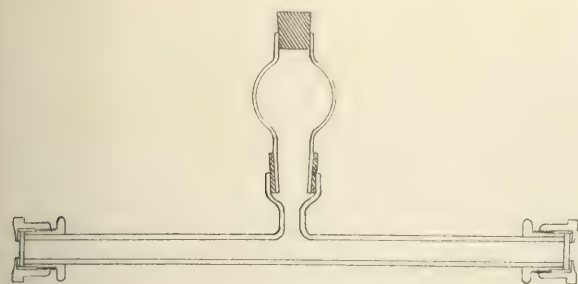


Fig. 1.

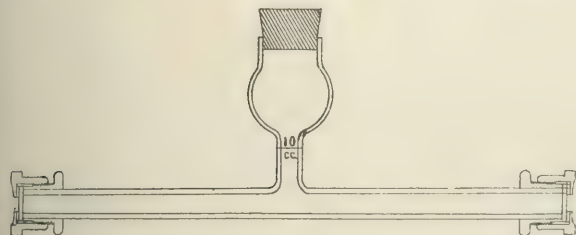


Fig. 2.

This device proved very serviceable also in making additions to solutions derived from syrups, to find the maximum rotatory power, as will be noted further on in this report. This method of procedure gave results more strictly comparable, except for the possible slight influence of volume or concentration, than those in Table I. This table brings out what is not clearly evident from Table I, that acetic acid alone, added in moderate quantity, can slightly increase the rotatory activity. As the quantity of potassium acetate is increased, the rotatory power gradually falls (tests Nos. 348 and 374), but a considerable proportion can be present without any reduction that in technical analysis need be considered very serious. With calcium acetate (Nos. 378 and 379) the effect is also a relatively slight lowering. With barium acetate (Nos. 376 and 377) the tests commenced with larger amounts, *viz.*, 1.6 cc. 20 per cent. solution or 320 mg. to 12 cc. or roughly 1.5 times the barium acetate equivalent of the malic acid. In the absence of free acetic acid, we find its depressing effect upon the rotatory power greater with a greater excess of uranium. With acetic acid in a quantity for maximum rotatory power, it polarizes 95.7 per cent. in No. 377 and 97 per cent. in No. 376 of what the same strength of malic acid solution without the barium salt does.

Referring again to Table I, we note that with all these additions of acids, excepting citric and possibly

the mixture of lactic and acetic acids, there is a range in the degrees of neutralization through which they do not interfere seriously. Can we find a general means of detecting this degree of neutrality and of establishing it in unknown mixtures containing these foreign acids with malic acid?

Looking through the series we find that the stronger the acids (in H ions) the lower the non-interference range in neutralization can reach. Thus free acetic acid shows less tendency to interfere than the stronger acids, formic and lactic. Succinic acid in this respect comes between acetic and lactic or formic. The three mineral acids are far more effective than the organic acids in interfering with the rotatory activity of the malic-acid-uranium compound. In their electrical conductivities, which may be taken as a measure of ionization and of concentration of H ions, these acids stand in the same order as in their interfering power, *viz.*, for normal solutions, hydrochloric (100), nitric (99.6), sulphuric (65.1), formic (1.68), lactic (1.04), succinic (0.581), and acetic (0.424).¹ In this list we find also citric (1.66) and malic (1.34) acids.

To study the relations between concentrations of H ions and rotatory activity and in analyses to establish a degree of acidity for maximum rotatory activity, an indicator, such as methyl orange, of low sensitiveness towards weak acids, may conveniently be used. Standard tints for comparison were established as exhibited in Table III.

TABLE III.

Standards of acidity or concentration of H ions, in tints with methyl orange. Each number has 10 cc. normal acetic acid, 2 drops of methyl orange solution and other additions as indicated, and is made up to 30 cc.

No. of stand- ard.	Additions.	No. of stand- ard.	Additions.
1	2 cc. normal H ₂ SO ₄	8	3.0 cc. normal KOH
2	Nothing	9	3.5 cc. normal KOH
3	0.5 cc. normal KOH	10	4.0 cc. normal KOH
4	1.0 cc. normal KOH	11	5.0 cc. normal KOH
5	1.5 cc. normal KOH	12	6.0 cc. normal KOH
6	2.0 cc. normal KOH	13	8.0 cc. normal KOH
7	2.5 cc. normal KOH	14	12.0 cc. normal KOH

Glancing through Table I for the cases in which the polarization reached its maximum, say from 28.00 up, we see that in no case where the acidity corresponds to No. 1, did it reach that limit, and that in nearly all cases where the acidity corresponded to Nos. 3 to 12, it reached this maximum. Very exceptional was the behavior with citric acid, line 7, and to a less extent also that of the combined addition of lactic and acetic acids, line 13. Since these were such striking exceptions, we seek the cause elsewhere than in the degree of acidity, and, sure enough, the addition of more uranyl acetate, lines 8, 9, 10 and 14, shows that the low results were due to an insufficiency in this reagent. Speculating upon the reason why these acids should require such a large proportion of uranyl acetate, we note that both the citric and the lactic acids are oxyacids and we recall in this connection that of the active dicarboxylic acids, it is also the oxyacids that show the remarkable sensitiveness to uranyl compounds in greatly increased optical activity. This points to the hypothesis that the uranyl group readily

¹ Ostwald's "Outline of General Chemistry," 1st ed., pp. 360-1.

enters the molecule at the alcohol hydroxyl, and that therefore the citric and the lactic acids have a power of using up the uranyl and holding it away from the malic acid, which the acetic, formic, succinic, etc., acids do not possess. This view would support the hypothesis of Walden,¹ who proposed the formula of the active acid with (UO_2OH) displacing the H of the alcoholic hydroxyl group, and it argues against the view held by Itzig,² that it displaces a carboxyl H.

In the polarization of malic acid the presence of other active dicarboxylic oxyacids not represented in these tables, since these themselves show marked changes in their optical activity on addition of a uranyl compound, must of course, cause an interference of a different kind than that caused by the acids here listed. Of these, tartaric acid will receive some consideration below under a practical method of estimation and under some notes on tartaric acid.

(b) *Sugars*.—In tests with the usual proportions of malic acid and uranyl compounds and with a sugar, it was found that the sugars (sucrose, dextrose and levulose were tried) had no appreciable influence upon the rotatory activity of the malic-acid-uranium compound, even though present to the extent of 3 per cent. or of five times the quantity of malic acid, the independent activity of the sugar used being, of course, taken into consideration. H. Grossman³ has studied in detail the action of uranyl compounds upon sugars and finds but slight changes, especially in the acid solution.

6. *Influence of the Time of Standing after Mixing Upon the Rotatory Power*.—Several hours have no notable influence, but several days cause a lowering.

7. *Influence of Temperature*.—Very careful tests, recorded in Table IV, indicate that the influence of the temperature is somewhat more than what is accounted for by the expansion of the water solution. The rotatory power for the same number of grams per 100 true cc. decreases as the temperature rises. In a 1 per cent. solution this is, on an average, 0.03 degrees Ventzke per degree C. rise in temperature.

TABLE IV.

Influence of temperature and kind of light used upon the rotatory power of the malic-acid-uranium compound. All numbers in line 1 were of the same solution, of a concentration of 0.11207 normal at 20°, and all those in lines 2 and 3 were of another solution, of a concentration of 0.10682 normal at 20°. In each number polarized below or above 20° a correction was made for the contraction or expansion from the volume at 20° and the polarization given in each case is that calculated for a solution at that temperature having 1 gram malic acid in 100 true cc.

No. of line	Light used	Temperature of polarization.						
		10°	15°	20°	25°	27.5°	30°	35°
1	Welsbach polarization	29.22	29.02	28.91
2	Welsbach polarization	30.04	29.96	29.72	29.56	29.35	29.30	29.15
3	Sodium polarization	28.99	28.95	28.84	28.60

8. *Influence of Heating when Mixing*.—Heating the mixture up to boiling (to hasten the solution of uranyl acetate) has no influence on the results.

9. *Influence of the Kind of Light Used in Polarizing*.—As before noted, with the intensely yellow or brown uranium compound in the polariscope, the field could

not be adjusted quite uniform in shade and color, thus showing a dispersion or absorption unlike that of the compensating quartz wedge. This is not enough to seriously interfere with the accuracy of the results, but to get data with the standard polariscopic light I also made parallel polarizations with sodium light (line 3, Table IV). Sharper readings can be made with a good sodium flame, and these readings run about 0.8° Ventzke lower for a 1 per cent. solution than with the white Welsbach light.

10. *Some Notes on the Tartaric-acid-uranium Compound*.—As other active dicarboxylic oxyacids also suffer marked changes in their optical activity by the addition of uranyl compounds, these must receive consideration in a scheme for the estimation of malic acid based upon such a change in optical activity. Of these *d*-tartaric acid is the most frequently associated with malic acid in natural products. Results from a limited number of tests indicate that *d*-tartaric acid follows similar laws to those with malic acid in that the activity of the uranium compound is independent of the kind of uranyl compound used, that somewhat more uranium is needed than in the ratio 1 : 1, and that small amounts of weak foreign acids do not interfere seriously. The tartaric-acid-uranium compound in a 1 per cent. solution has about 26.1 dextro-rotatory power as against 29.4 levo-rotatory power of a 1 per cent. malic acid solution. If, however, we compare molecularly equivalent strengths, *e. g.*, 0.1 *N*, they have remarkably nearly the same power, 19.6 for tartaric acid and —19.7 for malic acid. From the data the specific rotatory power of the free tartaric acid, with white light at 27.5° C., is

$$[\alpha]^{27.5} = 16.3$$

as against

$$[\alpha]_D^{20} = 14$$

usually given for yellow light at 20° C.

For the uranium compound, computed on the free tartaric acid, I find for white light and quartz compensation

$$[\alpha]^{27.5} = 453$$

as against the maximum

$$[\alpha]_D = 303$$

reported by Walden¹ for yellow light. I thus find a 28-fold increase instead of 20-fold, as reported by Walden.

II. METHOD FOR THE QUANTITATIVE DETERMINATION OF MALIC ACID AS FINALLY ADOPTED.

With the foregoing data before us we have the basis for establishing a quantitative method for estimating malic acid, based upon the change in its optical activity on conversion to the uranium compound, under the conditions for the maximum change. What preliminary preparation the substance needs, of course depends upon its composition.

1. *Procedure with Only Non-interfering Substances Present*.—This applies to solutions which may contain besides malic acid, *a*, neutral active or inactive substances, like the sugars in small quantities, or *b*, other

¹ Ber. d. chem. Ges., **30**, 2889 (1897).

² Ibid., **34**, 3822 (1901).

³ Z. d. Ver. deutsch. Zuckerind., **55**, II, 1058 (1905).

¹ Ber. d. chem. Ges., **30**, 2890 (1897).

acids in small quantities, say up to a strength of 0.2 *N* or to a strength not exceeding double that of the malic acid present if the latter is above 0.1 *N* (excepting optically active dicarboxylic oxyacids and acids destroying or precipitating either the malic acid or the uranyl compound). I shall consider two methods of procedure, of which one or the other will be preferred according to circumstances, such as the amount of solution available, the apparatus available, what is known concerning the composition of the solution and its condition as to acidity or alkalinity, etc.

(a) Procedure in which the proper degree of acidity for maximum rotatory power is established beforehand and the solution then polarized. The acids should be in the free state. If the solution is probably stronger than 0.2 *N* in malic acid, dilute preferably to a strength between 0.1 *N* and 0.2 *N*, making up to a definite volume. A convenient volume is 50 cc. To an aliquot part of it (say 10 cc.) add both methyl orange and phenolphthalein, then titrate with 0.1 *N* potassium hydroxide, noting the point between which the methyl orange passes through the shades between those of the two methyl orange standards, first, in $\frac{1}{3}$ *N* acetic acid and, second, in $\frac{1}{3}$ *N* acetic acid in which $\frac{1}{4}$ of the acid has been neutralized by potassium hydroxide. Note also the point at which the phenolphthalein shows complete neutralization. Unless the polarization tube is dry, rinse it with a little of the original solution, fill and polarize in the 20 cm. tube for the reading *P*. Return the portion from the polariscope tube to the main portion and take another aliquot portion (20 cc.) of this solution, add uranyl acetate in a quantity that will allow about 1 atom uranium to every atom of displaceable H of the acids (*i. e.*, about 0.046 g. Kahlbaum's crystalline uranyl acetate, containing about 51.6 per cent. uranium, for every cc. 0.1 *N* potassium hydroxide required for complete neutralization of this portion). Dissolve the uranyl acetate, then add potassium hydroxide in form of 0.1 *N* or *N* solution in the proportion necessary to secure a degree of neutralization within the range as determined in the above titration with methyl orange as indicator. Make up to definite volume (25 cc.). Filter through a dry filter, if necessary, and polarize in a 20 cm. tube. Increase the reading in the ratio that the volume of this portion was increased (by $\frac{1}{4}$, if 20 cc. were made up to 25 cc.) for the reading *P'*.

From the difference between the rotatory power with and without the uranyl acetate, *i. e.*, by the increase in the levo-rotation, calculate the malic acid, from the basis that in a 1 per cent. solution of malic acid, polarized in a 2 dcm. tube, at 20° C., the increase in levo-rotation is, with white light and quartz compensation, 29.6° Ventzke (or 10.25 circular degrees) and with yellow sodium light, 28.8° Ventzke (or 9.99 circular degrees). If the polarization was made at any other temperature than 20° C., correct this reading in degrees Ventzke by multiplying by $1 + 0.001(t - 20)$, in which *t* is the degrees C. Putting this into a formula and letting *t* = temperature C., *L* = length of polariscope tube in dcm., *P* = the

polarization of the mixture without uranium and *P'* = polarization of the same strength mixture with uranium, the formula for the per cent. malic acid in that strength solution is for white light—

(1) Per cent. malic acid

$$= \frac{(P' - P) \times [1 + 0.001(t - 20)]}{29.6 \times \frac{1}{L}}$$

or for yellow light

$$(2) = \frac{(P' - P) \times [1 + 0.001(t - 20)]}{28.8 \times \frac{1}{L}}$$

or for yellow light with the circular scale

$$= \frac{(P' - P) \times [1 + 0.001(t - 20)]}{9.99 \times \frac{1}{L}}$$

If the malic acid in 50 g. of the material analyzed is contained in a volume of 50 cc., as proposed below for syrups, and if 20 cc. of this solution are diluted to 25 cc. for polarizing and the reading increased by $\frac{1}{4}$ for *P'*, then to find the per cent. malic acid, multiply the difference in readings (*P' - P*), with the sign changed, by 0.0338 if white light and the Ventzke scale were used, by 0.347 if yellow light and the Ventzke scale were used, and with 0.1001 if yellow light and the circular scale were used. These constants are calculated for the temperature 20°. The correction for other room temperatures may be neglected in ordinary analyses.

Notes on the Above Method. 1.—If the acids are not all in the free state in the start, but are partly neutralized, so that the titration of a portion of the solution with phenolphthalein as indicator will not indicate the total acids, then the solution, after suitably neutralizing, may be divided into aliquot parts, adding to one portion a medium amount of uranyl acetate and to another equal portion, somewhat more uranyl acetate. Should the latter portion give higher results than the former, then additional portions may be treated with different amounts of uranyl acetate, until a maximum effect is produced. Or, more advantageously, a definite volume of the solution with a conservative amount of uranyl acetate in solution is introduced into a dry polarization tube provided with a tubulature. After polarizing, a small weighed quantity of wholly soluble, dry, crystalline uranyl acetate is added and, after dissolving, the solution again polarized. Allowing for an increase in volume of 0.04 cc. for every 0.1 gram uranyl acetate added, if the new reading is higher, then additional amounts of uranyl acetate are added, until a maximum effect is produced or the solution is cold saturated with uranyl acetate.

2. In case the test portion with methyl orange gives a shade of pure yellow or almost pure yellow, showing alkalinity, neutrality, or a point nearer neutrality than the shade of the second standard mentioned, then the titration may be made with 0.1 *N* acetic acid to a point within the range mentioned and a corresponding amount of acetic acid added to the main portion.

3. In case the original solution is colored so that the methyl orange shades are not pure, the neutralization of an excess of acidity may be carried to a stage

at which the color has distinctly begun to change, or in case of an alkaline solution, the neutralization in one portion is carried to a point where the change is complete, then in the portion to use it is stopped just before it is complete.

In the last two cases it is more advantageous to work according to the procedure next to be given.

(b) Procedure in which the proper acidity is established by trial polarizations after successive additions of alkali or acid. The solution of suitable strength is prepared, the polarization without uranyl is made, and the right amount of uranyl acetate is determined and added as in the preceding procedure. The polarization of the uranyl compound is made in a tube with a tubulature, to which is attached a tube or bulb-tube to increase its capacity, as previously described. Into this tube, previously dried, a measured volume of the solution is placed and polarized. To the mixture in the tube is added from a burette (preferably of small diameter) in successive portions of 0.5 cc. each, either double normal potassium hydroxide or double normal acetic acid solution, according as the original mixture is too strongly acid or too nearly neutral or alkaline, mixing and polarizing after each addition. When the maximum rotatory activity is reached and exceeded, allowing for the increase in volume when comparing the readings, this maximum, computed for the volume before dilution, is used to calculate the per cent. malic acid as directed in the previous procedure. A suitable conservative quantity of liquid by this method is 25 cc. If the liquid used in polarizing before adding the uranyl acetate is poured back, 20 cc. of the solution may remain to be pipetted into another 25 cc. flask and there treated with uranyl acetate and made up to 25 cc.

Notes on the Above Method.—In the majority of solutions from natural products to be examined for malic acid, I consider this second method more advantageous. In exceptional cases where each addition of the reagent (especially of potassium hydroxide) causes a precipitate which has to be filtered off before polarizing, this method can, of course, not be applied unmodified. Such a case I had in a solution of acids from cane syrup, prepared by use of the lead salts, and without the previous removal of phosphoric and possibly other acids that may form a precipitate with uranyl compounds. By choosing a different means of separating the malic acid (see below) I could avoid this admixture and use this latter method in the polarizing. Where many such polarizations are to be made, I would deem it expedient to provide one's self with a polarization tube that has a fixed volume marked on a suitable neck of the tubulature, which might conveniently be 10 cc. (see Fig. 2). Above this neck should be a bulb large enough to hold about 10 cc. additional, with a short neck large enough to admit of wiping the bulb dry inside above the mark, and this neck should be provided with a close-fitting rubber stopper. With such a tube and sufficient of the solution to be polarized, the necessity of drying the tube is avoided in that it may be rinsed with a portion of the solution, then filled to the mark, wiping away any

that may adhere to the inside walls above the mark.

2. *Procedure with Interfering Substances Present.*—Either of the above two general procedures, as shown by the preceding data, is applicable to a wide range of mixtures, yielding results very near the true value of the malic acid, when there is present even a considerable portion of such substances as the sugars, or acetic, lactic, succinic, citric, hydrochloric, nitric, or sulphuric acids. With certain other substances which interfere, or with very large amounts of these present there is necessary some preliminary operation to eliminate the interfering substances or to reduce the amount of foreign acids and neutral optically active substances. How most advantageously to make these separations and the details of any method will depend upon the nature of the accompanying substances, upon which of these it is desired also to determine, upon the apparatus and reagents available, and upon the urgency of economizing in sample, reagents, or time. What follows on this subject is meant rather in the way of data and suggestions than in the hope of describing in detail a method that will be the most advantageous for any wide range of natural products. In the next section will then be described, in detail, methods for syrups based upon the data.

From an excessive amount of sugars, of acetic or nitric acids, or of other bases, the malic acid may readily be separated as a lead salt and afterwards set free by hydrogen sulphide. The tartaric acid may be removed more or less nearly completely as the acid potassium tartrate, the calcium tartrate, or the barium tartrate. To test the efficiency of several proposed methods for separating malic acid from sugar (in syrups, cane juice, etc.) and to work out the details of methods, I carried out a series of tests on its precipitation as lead, barium, and calcium salts with various amounts of alcohol.

It is generally assumed by analysts and writers of text-books on organic analysis that lead acetate or subacetate, and a volume of alcohol equal to that of the original solution, would precipitate quantitatively a group of organic acids, including malic acid. A series of tests made by me does not bear out this assumption, and the loss is especially great, 18 per cent., with sugar solutions. S. H. Ross,¹ in his study of the Winton "lead number" method of distinguishing between pure and adulterated maple products, also noted a tendency of sugar solutions to hold back lead. He proposed to "correct the solvent action of the sugar" by the addition of a small quantity of potassium sulphate. I find that with the addition of the proportion of potassium sulphate recommended by Ross, and lead-subacetate in limited quantity, but more than enough for the malic acid present, the loss of malic acid increases to 67.2 per cent. when no alcohol is used, and 38.5 per cent. when 1.8 volumes of alcohol is used. These facts suggest that probably in the experiments of Ross the potassium sulphate improved the results, not by correcting the incomplete precipitation of certain constituents of the syrup, but rather by compensating for it, and that therefore a numerical

¹ Circular 53, Bureau of Chemistry, U. S. Dept. of Agr., p. 8.

addition to the results, corresponding to the solubility of the lead precipitate in a sugar solution of equal strength, would answer the purpose quite as well.

For complete precipitation of malic acid from sugar solutions with lead acetate or subacetate, more alcohol is needed than an equal volume. 3.6 volumes of 95 per cent. alcohol with an excess of lead acetate (27.8 grams sugar, 35 cc. water, 0.1605 gram malic acid, 1.5 cc. lead acetate solution of specific gravity 1.25, and 125 cc. of 95 per cent. alcohol) effected an almost complete (98 per cent.) precipitation of the lead malate, as determined by the polariscopic method after liberating the acid from the lead by means of hydrogen sulphide. The subacetate was found not quite so advantageous. In certain tests with maple syrup in which only one volume of alcohol was used in the precipitation with lead acetate, the results were 0.04 per cent. lower, thus showing a loss of about 7 per cent. of the malic acid present. In a series of tests with lead acetate as precipitant, having decreasing amounts of sugar, but with the sum of sugar plus water the same, the more dilute solutions showed the highest losses of malic acid.

Of calcium acetate and barium acetate in equivalent amounts and with like amounts of alcohol, the latter gave the more nearly complete precipitation, the results with the barium acetate and 14 volumes of 95 per cent. alcohol (27.8 grams sugar, 29 cc. water, 0.1537 gram malic acid, 8.3 cc. 16.2 per cent. barium acetate solution, and 414 cc. 95 per cent. alcohol) being apparently as good as those with lead acetate and 3.6 volumes of alcohol. In reality the precipitation with barium acetate in tests made was probably more nearly complete than that with the lead, the low results being accounted for in the slight depressing effect of the by-product, potassium acetate, which was present when polarizing the uranium-malic-acid compound. However, the recovery by either method is sufficiently near complete to serve ordinary practical purposes. Either method would effect a separation with but insignificant loss, of malic acid from sugars or nitric and acetic acids. By the barium acetate method of precipitation and subsequent solution in water we may at the same time separate it from hydrochloric and lactic acids, which would not be precipitated; from sulphuric, phosphoric, or oxalic acids, whose barium salts are insoluble in water; and from interfering excesses of succinic and citric acids, whose barium salts are difficultly soluble in water. If much tartaric acid were present, it would mostly be separated in the same operation. Similar advantages for separation from these other acids are possessed by calcium acetate. Tests with aconitic acid showed that its calcium salt is soluble in cold water but is precipitated almost completely by the addition of an equal volume of alcohol, while calcium malate solutions of strengths up to 0.25 per cent. were not precipitated by the addition of an equal volume of alcohol.

Tests on the precipitability of tartaric acid as a calcium salt, by the addition of an equal volume of alcohol, showed that when exactly neutralized with calcium hydrate, using phenolphthalein as indicator,

then an excess of calcium acetate and an equal volume of absolute alcohol added, there remained in 100 cc. of the supernatant liquor after standing over night 0.0076 gram calcium tartrate, equivalent to 0.0060 gram tartaric acid.

If this method of separating malic acid is applied to mixtures including tartaric acid, approximate corrections in the subsequent polarizations of the malic acid before and after the addition of uranium for the traces of tartaric acid would be 0.01 and 0.3 degree Ventzke, respectively, to be subtracted from P and P' in the formula, for every 100 cc. of the 50 per cent. alcoholic filtrate finally concentrated into 50 cc. for polarizing.

III. SEPARATION OF MALIC ACID FROM CANE AND MAPLE SYRUPS AND SUGARS AND ITS DETERMINATION BY THE POLARISCOPIC METHOD.

Based upon the data in the preceding sections and upon further facts developed in the examination of syrups as reported below, I recommend either of the following two methods:

1. *Lead Acetate Method.*—Determine the acidity of the sample by diluting 5 cc. of it with water, adding phenolphthalein, and titrating with 0.1 N alkali. Weigh out 50 grams of the syrup (or $33\frac{1}{3}$ grams of sugar, adding to it $16\frac{2}{3}$ cc. additional of water). Add to it the necessary amount, as previously determined, of normal or double normal alkali to neutralize the acidity and enough water to make with the added alkali solution 15 cc. After mixing thoroughly (or dissolving in case of sugar), add 10 cc. of lead acetate solution of specific gravity 1.25. Add 150 cc. neutral 95 per cent. alcohol. Shake thoroughly and set aside for three hours or more. Carefully decant the clear supernatant liquor through a suction filter of a diameter of not less than 7 cm. Remove the clear decanted filtrate from the filtration flask, then bring the precipitate itself onto the filter. After it runs clear, pour back onto the filter what at first ran through cloudy and rinse the filtration flask with some of the decanted clear liquor, returning the rinsings onto the filter, then continue the filtration, finally rinsing the precipitation flask and precipitate a few times with 75 per cent. alcohol. Thorough washing is unnecessary. Return the precipitate and filter into the precipitation flask, heat with some water, and shake to disintegrate the precipitate, then treat with hydrogen sulphide to convert the lead into lead sulphide. Repeat the heating and shaking and the treatment with hydrogen sulphide, if necessary, until the whole of the precipitate is acted upon. The precipitate tends to cake during filtration, often causing difficulty in disintegrating it, so that it will be acted upon by the hydrogen sulphide. Filter hot and wash with hot water containing some hydrogen sulphide. Concentrate the filtrate on the water bath to about 30 cc., transfer to a 50 cc. flask and make up to the mark. Determine in this solution the malic acid according to either of the methods given in Section III, Division 1, of this report. Use about 0.7 gram uranyl acetate with 20 cc. of this solution.

Notes on this Method.—(a) If the solution is too dark colored to polarize in the 20 cm. tube, either

before or after the addition of the uranyl acetate, use a 10 cm. tube or dilute a portion. In four samples of maple syrup which I examined, three of which were unusually dark, I was able to polarize any of them in the 20 cm. tube without further dilution than here planned. In a sample of very dark cane syrup I had to use the 10 cm. tube in order to be able to polarize it. With ordinary light colored syrups or sugars the solution might safely be made twice as strong, *i. e.*, the acids from 50 grams syrup concentrated into 25 cc.

(b) If the analyst does not object to the greater care necessary in working with smaller volumes, he can very well make the determinations with only 25 cc. of solution, in which case half the above quantities of substance and of reagents will suffice, thus saving time in filtering.

(c) The 0.7 gram uranyl acetate is deemed a safe margin of excess for 20 cc. of the above strength solution of acids from maple or cane syrups. It is twice the theoretical amount needed, if the syrup has 0.50 per cent. malic acid, and if the uranyl acetate has 51.56 per cent. uranium.

(d) Where no acids other than those separated from maple products need be expected, the titration of an aliquot part of the solution of the acids may be omitted, since maple products do not yield any interfering strong mineral acids. The cane syrups, however, which I examined had considerable phosphoric and some sulphuric acid, hence the solutions required some alkali for the maximum rotatory power. Because of these, it was more advantageous with cane syrup to use the second method of separating the malic acid, to be described in the next paragraph.

2. *Barium Acetate Method.*—Determine the acidity as in the lead acetate method. Weigh out 25 grams of syrup (or $16\frac{2}{3}$ grams sugar, adding to it $8\frac{1}{3}$ cc. additional of water). If the acidity was more than a trace, about neutralize with the required amount of powdered barium hydroxide, avoiding an excess (0.0157 gram $\text{Ba}(\text{OH})_2 + 8\text{aq.}$ for every 1 cc. 0.1 N alkali required by the 25 grams of syrup). Add 7.5 cc. 20 per cent. barium acetate solution. Mix and dissolve the barium hydroxide (and the sugar in case a sugar is analyzed). Now add 220 cc. 95 per cent. neutral alcohol and warm on the water bath to incipient boiling, in a flask (preferably Erlenmeyer) provided with a reflux air-condenser, until the precipitate settles readily and the supernatant liquor is clear or nearly clear. About one hour suffices. Decant carefully as far as possible the hot liquor through a filter. Dilute the liquid remaining with some of a hot mixture of 1 part water to 14 parts 95 per cent. alcohol and bring it upon the filter. Rinse as rapidly as possible the precipitation flask and the precipitate three or four times with this strength alcohol (thorough washing is unnecessary), then return the precipitate together with the filter to the precipitation flask, dissolve in about 20 cc. hot water, filter, and wash with hot water. To the filtrate add 1 cc. double normal acetic acid, then concentrate to about 10 cc. Add 2 cc. additional of double normal acetic acid, transfer to a 25 cc. flask, filtering if necessary, and make up to the mark. Determine the

malic acid by the second of the methods described in Section III, Division 1, of this report, adding more acetic acid, if necessary for the maximum rotatory power.

Notes on the Latter of the Above Methods.—(a) As already noted, this method effects also the separation of the sulphuric and the phosphoric acids, which are likely to occur in cane syrup.

(b) The smaller amount of material, 25 grams, is here recommended in order to save alcohol and time in filtering, but if preferred, more liberal quantities may be used, say 50 grams, making up the solution for polarizing also to 50 cc. The first filtering is advantageously accomplished by use of a long-stemmed hot-water funnel. A very efficient hot-water funnel may be improvised by putting a small long-stemmed funnel inside a larger short-stemmed funnel, with hot water in the outer funnel, siphoning off the water from time to time and replacing with hot water. If the alcoholic liquor is allowed to cool, it may yield crystals of sugar, which are then difficult to dissolve in the alcoholic wash liquor.

(c) It should be noted that the alcohol for any of these separations should be neutral. The commercial 95 per cent. alcohol is sometimes contaminated with free (volatile) acids to such an extent as to make it necessary to neutralize (conveniently with sodium carbonate) and redistil before using.

(d) Care should be exercised not to render the liquid alkaline, as this would be conducive to developing highly colored decomposition products out of the sugars. For the same reason it is best to acidify the water solution of the barium salts before concentrating, and for the additional purpose, that the main part of the sucrose remaining may be inverted so that it will not undergo a change in optical activity during the interval between the polarization without and with the uranium.

(e) According to the results in Table II, the polarizations in the presence of the barium compounds are a little low. This suggests that the results might be improved by introducing a correction factor of about 1.03.

3. *Results from Some Cane and Maple Syrups.*—Malic acid was separated from two samples of cane and four authentic samples of maple syrups by both the lead acetate and the barium acetate methods and estimated polariscopically by the second method given. The results are set forth in Table V.

The clarification of Cane Syrup I was accomplished with sulphur dioxide, followed by liming back to near neutrality. At the time of making these tests it had undergone a slight fermentation. Maple Syrup IV was produced from the sap of soft maple trees; the others from sap of hard maple trees. A partial clarification was effected in the manufacture of the maple syrups by mixing an egg or the white of an egg to every four or five gallons of thin syrup, then skimming off after coagulation during boiling. The syrups had been freed by decantation from the so-called "sugar sand" which is always formed in the concentration of the sap. After the separation of the acids from the sam-

ples of maple syrup by the lead acetate method, the free acids required no further neutralization to secure the maximum rotatory activity of the uranium compound, there being no strong mineral acids present.

TABLE V.—MALIC ACID DETERMINATIONS IN CANE AND MAPLE SYRUPS AND IN MIXTURES OF THESE

Syrup and its source.	Degrees Brix.	Per cent. sucrose, single polarization.	Apparent purity (per cent.).	Color.	Per cent. malic acid.	
					By lead acetate method.	By calcium acetate method.
Cane I, La. Sugar Experiment Station.....	67.3	53.3	79	Dark	0.04 ¹	0.04 ¹
Cane II, Local Manufacturer	71.5	54.4	80	Medium	0.01	0.02
Maple I, A. H. Miller, Goshen Ind.....	68.7	60.0	90	Light	0.46	0.49
Maple II, M. A. Yoder, Middlebury, Ind.....	68.2	61.0	89	Dark	0.29	0.32
Maple III, M. A. Yoder, Middlebury, Ind.....	70.8	..	Dark	0.25	0.26
Maple IV, D. R. Yoder, Goshen, Ind.....	34.0	..	Dark	0.53	0.51
Mixture, 1 part Cane I and 1 part Maple I.....	0.26	0.26
Mixture, 3 parts Cane I and 1 part Maple I.....	0.13	0.13

4. *Detection of Adulterations of Maple Products by the Determination of the Malic Acid by this Polariscopic Method.*—Since the maple products are distinguished by a relatively high percentage of malic acid (0.26 per cent. to 0.53 per cent. in the samples examined), we have by its determination a chemical means of distinguishing it from such substances as cane syrup or impure cane sugar, and to the extent that we can establish a normal by the examination of many samples of maple syrup or sugar from various sources; to that extent we can use the results in judging of the purity of the product, as far as adulteration with pure sugars is concerned. Tests with mixtures of cane and maple syrups give results agreeing sufficiently nearly with the amount of malic acid calculated for the mixture to make it apparent that this method of examination will also afford us a means of determining approximately the proportion of each in a mixture of maple syrup or sugar of known malic acid content, and precipitate-forming substances having little or no malic acid, such as cane syrup or impure cane sugar. More work needs to be done on samples of maple syrup and sugar to ascertain whether such a normal can be established.

For comparison, the "malic acid value" was also determined in Cane I and Maple I syrups by precipitation with calcium acetate, ignition of the precipitate, and calculating the malic acid from the alkalinity of the ash. This gave for Cane I, 1.22 and for Maple I, 0.59. That the "lead number" by Winton's or Hortvet's method would also have been higher in the cane than in the maple syrup could be seen by the bulks of the lead precipitates formed in the procedure for separating the malic acid.

5. *Application of the Methods of Separation and Determination of Malic Acid to Other Products.*—Fresh apple juice and various other natural products are

¹ Sample had started fermenting. An earlier test showed only 0.02 per cent. malic acid.

distinguished by their malic acid content. It is therefore probable that this method may be adapted to distinguishing these from their imitations and adulterations. In many other natural products no reliable differentiations have been made of the organic acids present, and it is not improbable that now, with a more delicate method at hand for detecting and determining malic acid, its presence or absence, and its quantity in these may be ascertained and may be found to be a useful means of identifying them or distinguishing between them.

IV. A SIMILAR POLARISCOPIC METHOD FOR THE ESTIMATION OF TARTARIC ACID.

A similar method for tartaric acid can evidently be based upon the change produced in its rotatory power by uranyl compounds. Basing formulas for calculating the per cent. tartaric acid in the solutions polarized upon the specific rotatory powers as found in these experiments, for white light and quartz compensation, *viz.*, $[a]^{27.5} = 16.3$ for the free acid and $[a]^{27.5} = 453$ for the same converted to the uranium compound, using the Ventzke scale,

$$\text{Per cent. tartaric acid} = \frac{P' - P}{25.16 \times \frac{1}{l} \times \frac{1}{2} L}$$

V. DETERMINATION OF TARTARIC AND MALIC ACIDS IN A MIXTURE OF THE TWO.

Evidently, if in a mixture of these two acids another value besides the rotatory power can be determined, we have the basis for calculating the amount of each present. Thus, if we can determine the total acidity in terms of normal acid due to these two acids and the change in its polarization by treatment with an excess of uranyl acetate, we may develop the formula to calculate the amount of each acid as follows:

Let x = grams malic acid in 100 cc. of the solution.

Let y = grams tartaric acid in 100 cc. of the solution.

Let n = total cc. normal alkali required to neutralize these acids in 100 cc. of the solution.

Let m = change in polarization in a 20 cm. tube in degrees Ventzke occasioned by the uranyl compound. Then

$$n = \frac{x}{0.06703} + \frac{y}{0.07503},$$

and if we take the rotatory power at 27.5° C., *i. e.*, a change of -29.27 in a 1 per cent. malic acid solution and a change of 25.16 in a 1 per cent tartaric acid solution, then

$$m = 25.16y - 29.27x.$$

From these two equations we derive

$$x = 0.03287n - 0.01741m, \text{ and}$$

$$y = 0.03824n + 0.01949m$$

VI. ACKNOWLEDGMENTS.

The foregoing investigation was commenced by me during my engagement with the Louisiana Sugar Experiment Station at Audubon Park, New Orleans, and later continued in private, and this report formulated, using by permission the data collected while in the service of the Experiment Station as well as those collected since. I wish also to acknowledge the faith-

ful services of Mr. W. G. Taggart, assistant chemist, in carrying out under my direction some preliminary experiments in this problem, leading up to those here reported.

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COCONUT OIL OF HIGH IODINE VALUE.

By W. D. RICHARDSON.

Received July 3, 1911.

Recently several shipments of alleged coconut oil were received by a large concern, and these shipments when analyzed gave iodine values of 18, 20, 24 and 21 respectively. A little later another shipment of alleged coconut oil was received by the same concern from another manufacturer, and this oil showed an iodine value of 20.

One of the principal chemical characteristics of the ordinary coconut oil of commerce, pressed from copra, is its low iodine absorption, the iodine number in a large number of instances being very close to 8 per cent. When, therefore, the high iodine values were found, in the cases of the shipments referred to, an investigation was started, which resulted in finding the cause of the high iodine values.

It was found that the oil in question came from two manufacturers, both located in the United States. Both of these manufacturers, upon being questioned, stated that their oil was pure coconut oil and that nothing but coconuts were used in its preparation. Upon being questioned further they both admitted that their oil was not pressed entirely from copra, but that considerable proportions of the waste material from desiccated coconut factories entered their presses. They stated that they used no unusual methods or extreme temperatures in the preparation of their oil and they failed to understand the reason for their oil showing different constants from the ordinary oil of commerce.

The waste material from the desiccated coconut factories consisted of parings of the rind from the coconut meats, and when this fact was ascertained it was thought best to procure some fresh coconuts and extract the oil from the meats and from the rind, in order to determine whether or not any difference in the oils from the two tissues existed. Accordingly a dozen coconuts were purchased, opened and the rind pared off from the meats. Both lots of the material were then dried separately at low temperatures and the oil extracted by means of ether. The following results were obtained:

	Iodine number.	
	Per cent.	Titer ° C.
Oil extracted from the meats of coconuts. . . .	8.90	23.3
Oil extracted from the rind.	40.25	25.5

The other constants, such as saponification number, were found to be identical with those obtained in the case of the ordinary coconut oil of commerce. The titer, as shown by the above figures, is slightly higher in the case of the coconut oil from the rind. These figures plainly indicate a considerable difference in composition between the oil from the rind of the

coconut meats and from the meats themselves. The rind is such a small percentage of the whole kernel that in all probability the oil derived from this source does not affect to any considerable extent the ordinary oil pressed from copra. On the other hand, when considerable quantities of parings are pressed, either separately or mixed with copra, the iodine value of the resulting oil is considerably increased.

These results are of importance inasmuch as the oils which would be most likely to be used for adulterating coconut oil, would have the same effect upon the ordinary coconut oil of commerce, as does the coconut oil from the rinds.

The present case appears to be another instance of the well-known phenomenon of vegetable physiology, that adjacent tissues in plants may contain oils of very different composition—a fact which is well exemplified in the case of palm oil and palm kernel oil.

The above results indicate that a coconut oil of relatively high iodine value is not necessarily adulterated by a foreign oil, although it can hardly be known as "coconut oil" in the ordinary commercial sense of the term, inasmuch as coconut oil has long been understood in commerce to mean an oil pressed from copra, that is, the whole dried coconut meat.

It was thought that the above facts were of sufficient interest to the oil and fat industries to warrant publication.

LABORATORY OF SWIFT & COMPANY, CHICAGO.

DETERMINATION OF VANADIUM IN STEEL AND IRON.

By B. O. CRITES.

Received June 7, 1911.

The determination of vanadium in steel carrying this element in amounts varying from 0.05 per cent. to 0.75 per cent. has been a problem commanding the attention of many of iron and steel chemists for several years.

The methods given in the earlier editions of books on iron and steel analysis have been found almost wholly impracticable and those appearing in the more recent literature have neglected to give any very comprehensive idea of their accuracy or limits of accuracy.

Realizing the difficulties involved in the estimation of rather minute quantities of vanadium in presence of large amounts of iron, it is not the intention of the writer to severely criticize the work of other chemists in their efforts to produce satisfactory methods, but it seems that a discussion of the subject might be of interest at least to chemists who have had only limited experience with this determination.

A method said to have been used by J. Kent Smith in his extensive work on vanadium was first tried by the writer, the method in brief which was as follows:

Four grams of steel were dissolved in sulphuric and nitric acids, the tungsten being separated by the usual methods if present. The nitric acid was expelled by evaporation to the appearance of sulphuric acid fumes, then after dissolving the salts in water, chro-

mium and vanadium were oxidized with slight excess of potassium permanganate solution. After boiling, the excess of potassium permanganate was reduced with manganese sulphate, and the solution made up to a definite volume, filtered, and an aliquot part of the filtrate taken for titration—chromium being titrated with ferrous sulphate and potassium permanganate and finally the vanadium with ferrous sulphate and potassium bichromate. The principle underlying the method is that the vanadium is reduced by ferrous sulphate and oxidized by potassium permanganate in dilute solution but not by potassium bichromate.

After a number of attempts the method was finally abandoned. The end reaction being rather indefinite, there frequently was considerable doubt in the mind of the operator whether any vanadium was present or not.

A method described by Blair¹ was next tried. By this method the vanadium was separated from the iron by fusion with sodium carbonate and sodium nitrate, extraction of the vanadium with water and precipitation from slightly acid solution with mercuric oxide and mercurous nitrate. This precipitate was redissolved and the vanadium finally precipitated with ammonium chloride as directed. The results were unsatisfactory and this method was also abandoned.

The writer then endeavored to work out for himself the details of a method, suggested I believe by Roscoe, which might at least show whether vanadium really was present and the amount.

The method used was as follows:

Five grams of steel were dissolved in nitric acid which was then replaced by hydrochloric acid (tungsten being separated as usual if present) and an ether separation was made to separate the major portion of the iron; the vanadium in the water layer was separated from the iron remaining by large excess of sodium hydroxide, after first replacing hydrochloric with nitric acid. The caustic mixture containing precipitated iron was made up to a definite volume and an aliquot part of the filtrate containing the vanadium acidified and the vanadium precipitated by lead acetate and sodium acetate. The lead vanadate in turn was filtered off, dissolved in hydrochloric acid and evaporated to the appearance of fumes after adding a few cubic centimeters of sulphuric acid. Lead sulphate was filtered off and the vanadium in the filtrate was titrated with $N/100$ potassium permanganate solution.

In order to test its accuracy a standard solution of vanadium was prepared from divanadyl tetrachloride obtained from Eimer & Amend. The solution was standardized as follows:

The contents of a $\frac{1}{8}$ -ounce bottle of vanadium chloride (divanadyl tetrachloride), $2\text{VO}_2 \cdot 4\text{HCl} \cdot 3\text{H}_2\text{O}$, containing 4.051 grams were diluted to 2000 cc.

Twenty cubic centimeters of this solution were withdrawn, 5 cc. strong sulphuric and 40 cc. strong hydrochloric acid added, the solution was boiled down till it fumed strongly, then cooled, diluted to

150 cc. with water, heated to 80°C . and titrated with standard potassium permanganate solution, of which each cubic centimeter was equal to 0.005 gram iron or 0.004578 gram vanadium.

Measured amounts of this solution were then added to plain carbon steel, also to chrome and molybdenum steel and the samples were carried through by the method as described, with the following results:

Vanadium added. Per cent.	Vanadium found. Per cent.	Difference. Per cent.
0.03	0.03	0.00
0.06	0.06	0.00
0.06	0.05	-0.01
0.13	0.12	-0.01
0.13	0.14	+0.01
0.26	0.22	-0.04
0.26	0.24	-0.02
0.26	0.19	-0.07
0.10	0.09	-0.01
0.10	0.08	-0.02
0.10	0.07	-0.03
0.10	0.08	-0.02
0.10	0.10	-0.00
0.10	0.07	-0.03

Attempts to apply the method on samples to which over 0.30 per cent. vanadium was added showed decidedly low results. In such cases it was necessary to fuse the sodium hydroxide precipitate with sodium carbonate and potassium nitrate and determine the vanadium in the water extract, thus complicating the method. While not entirely satisfactory, the results were a very considerable improvement on anything obtained so far by other methods used.

Several months later Blair¹ published a method along somewhat similar lines but with a number of improvements and changes. He made two separations with ether instead of one and omitted the separation of lead sulphate by filtration, this being found unnecessary; a stronger solution of potassium permanganate was also used for the titration. After some practice with the method it was adopted as the best tried so far. The method even in its improved form was still somewhat lengthy and required considerable care in order to obtain anything approaching accurate results. A few of the results obtained are as follows:

Sample.	Vanadium added. Per cent.	Vanadium found. Per cent.	Difference. Per cent.
Carbon steel.....	0.75	0.78	+0.03
Chrome nickel steel.....	0.28	0.25	-0.03
Chrome tungsten steel.....	0.195	0.18	-0.015

The principal difficulty was in the analysis of high chromium steels; the chromium seemed to be very difficult to precipitate completely and would often be carried into the vanadium filtrate and thus complicate matters; also, small quantities of organic matter, probably from the filters used seemed to affect the results. These difficulties, of course, could be overcome, but they required considerable care.

C. M. Johnson published a method² about this time which was somewhat on the principle of the method used by J. Kent Smith, and described in the beginning of this paper. He omits, however, the use of manga-

¹ "Chemical Analysis of Iron and Steel," 6th Ed., p. 202.

² *J. Am. Chem. Soc.*, **30**, 1229 (1908).

² "Chemical Analysis of Special Steels, etc.," p. 8.

nese sulphate to remove excess of potassium permanganate and uses potassium ferricyanide in the solution instead of externally as an indicator. In the judgment of the writer, this is the most practical method available at present. The method as used in our laboratory is practically the same described by Johnson. Two grams of steel are dissolved in dilute sulphuric acid, heated with nitric acid, until the insoluble becomes a bright yellow, if tungsten be present, otherwise simply to oxidize the iron. The solution is diluted, brought to boiling and 3 per cent. potassium permanganate solution added until precipitate of manganese oxide remains after 20 minutes' boiling. This is very important, otherwise low results will be obtained. After cooling, the solution is filtered through asbestos¹ into heavy suction flasks and residue is washed with minimum quantity of very dilute sulphuric acid. The volume of the filtrate must not exceed 300 cc. The end reactions in the titrations to follow will be indefinite if solution is too dilute. The filtrate must be perfectly clear.

The titration of the chromium is the next operation; this is conducted as described by Johnson but it is important to add the standard potassium permanganate until an unmistakable pink persists after 30 seconds' stirring. The oxidation of the vanadium is sometimes a little slow at this point and permanganate must be added till the operator is certain there is a slight excess. The writer uses a solution of potassium permanganate, each cubic centimeter of which is equal to 0.005 gram iron. *N*/10 ammonium ferrous sulphate is used.

The calculation for chromium is as follows:

cc. KMnO_4 equal to FeSO_4 required for reducing chromium $\times 0.005$ (Fe value) $\times 0.311 \div 2 \times 100$ equals per cent. chromium.

The volume of the solution now ready for vanadium titration must not be over 350 to 375 cc. One cubic centimeter of a solution of potassium ferricyanide containing 0.020 gram of the salt in 20 cc. of water is added, then standard ammonium ferrous sulphate (same as used for chromium) till the end point is reached. It is well from time to time, during the titration, to add a drop or two of the indicator and note whether a green coloration is produced at a point where the drop mixes with the solution.

A blank should always be run on a steel of similar composition to the sample but without vanadium, and proper deduction made. A standard steel of composition similar to the sample, and to which a definite amount of standard vanadium solution has been added, should also be carried along with the unknown.

Inasmuch as the method described above shows accurately the amount of chromium present in the sample, and separate nickel determination, if nickel be present, can readily be made by the dimethylglyoxime or other of the well-known methods, there is usually no difficulty in preparing synthetic standards and blank of composition similar to the sample under

examination, at least sufficiently close for the purpose.¹

Sample calculation for vanadium:

10 cc. FeSO_4 diluted with H_2O and titrated with KMnO_4 required 8.5 cc.

1 cc. $\text{KMnO}_4 = 0.005$ gram Fe = 0.004578 gram Va.

Blank required 0.7 cc. FeSO_4 .

Sample required 2.3 cc. FeSO_4 .

2.3 — 0.7 = 1.6 cc. FeSO_4 required for the vanadium.

$1.6 \times 0.85 = 1.36$ cc. FeSO_4 (corrected) required for vanadium.

$\frac{1.36 \times 0.004578 \times 100}{2} = 0.31$ per cent. vanadium.

0.31 per cent. + 5 per cent correction = 0.325 per cent. vanadium.

A few of the results obtained are given below. There seems to be a tendency towards low results, especially in the higher figures. This may be due to a secondary reaction referred to by W. F. Bleeker² in his article on vanadium. "If a solution of hypovanadic acid or its salts be added to a solution containing ferric iron, the presence of ferrous iron is immediately observable. According to this we should expect low results, owing to the mass action of the reduced vanadium upon the ferric iron, giving a test for ferrous iron before the vanadium is all reduced."

The results obtained by the writer were about 5 per cent. low. However, if this correction of 5 per cent. is made, a very fair agreement is found. The method is quickly carried through and the end points are sharp.

Sample.	Added vanadium. Per cent.	Found vanadium. Per cent.	Difference. cent.	Corrected by 5 per cent. Per cent.
Plain carbon steel.....	0.11	0.123	+0.013	0.129
+0.11 per cent. vanadium.....	0.11	0.123	+0.013	0.129
Carbon steel.....
+1 per cent. molybdenum.....	0.55	0.519	—0.031	05.44
+0.55 per cent. vanadium.....	0.55	0.506	—0.044	05.31
Chrome nickel steel.....	0.33	0.309	—0.021	0.324
+0.33 per cent. vanadium.....	0.33	0.309	—0.021	0.324
Chrome tungsten steel.....	0.22	0.21	—0.01	0.22
+0.22 per cent. vanadium.....	0.22	0.222	+0.002	0.233
Carbon steel.....
+0.65 per cent. vanadium.....	0.65	0.63	—0.02	0.661
Carbon steel.....
+0.33 per cent. vanadium.....	0.33	0.314	—0.016	0.329
Chrome steel.....
+0.46 per cent. vanadium.....	0.46	0.46	0.00	0.483
Chrome tungsten steel.....
+0.529 per cent. vanadium.....	0.529	0.508	—0.021	0.533
Chrome tungsten steel.....
+0.46 per cent. vanadium.....	0.46	0.42	—0.04	0.441

A number of tests were made by both the Blair and Johnson methods, with results as follows:

¹ In this connection it might be well to call attention to the method described by N. M. Randall (*Mel. Chem. Eng.*, **8**, 17 (1910)), for quick estimation of chromium in chrome steels and chrome nickel steels and also the method of H. Wdowiszewski (*Chem.-Ztg.*, **34**, 1365) (*C. A.*, **5**, 1378) for chrome in chrome tungsten steels. Both of these methods give excellent results in a remarkably short time.

² *Mel. Chem. Eng.*, **9**, 209 (1911).

¹ The asbestos should be previously prepared in quantity by ignition in a muffle and washing with water.

Sample.	Blair method, vanadium, per cent.	Johnson method, vanadium, per cent.	Difference, per cent.	Johnson corrected by per cent. vanadium, per cent.
Chrome tungsten vanadium steel.	0.29	0.287	0.003	0.301
Vanadium steel.....	{ 0.25	0.208	0.042	0.218
	{ 0.25	0.225	0.025	0.236
Vanadium steel.....	{ 0.25	0.225	0.025	0.236
	{ 0.25	0.225	0.025	0.236
Chrome tungsten vanadium steel.	{ 0.75	0.705	0.045	0.74
	{ 0.76	0.72	0.04	0.756
Vanadium steel.....	0.61	0.60	0.01	0.63

Other methods, such as Campbell and Woodham's,¹ in which iron is largely separated from vanadium by converting iron into ferrous sulphate and crystallizing out with strong alcohol and methods described by Auchy² were either not as readily applicable as the Johnson method or were not successful in the writer's laboratory. Colorimetric methods, such as described by Slawik,³ were also unsuccessful.

The Johnson method may be used for the determination of vanadium in iron if it be modified to the extent of fusing with alkali carbonate and a little nitrate, the graphite and silica left insoluble when the iron is dissolved, on account of their tendency to carry vanadium. A blank and standard of similar composition should also be run.

Results on vanadium in iron by Johnson's method (modified).

	Per cent. added. Vanadium.	Per cent. found. Vanadium.	Per cent. Difference.	Per cent. Corrected.
Cast iron.....	0.22	0.21	0.01	0.22
Malleable iron....	0.23	0.21	0.02	0.22

LABORATORY OF OSCAR TEXTOR,
CLEVELAND, O.

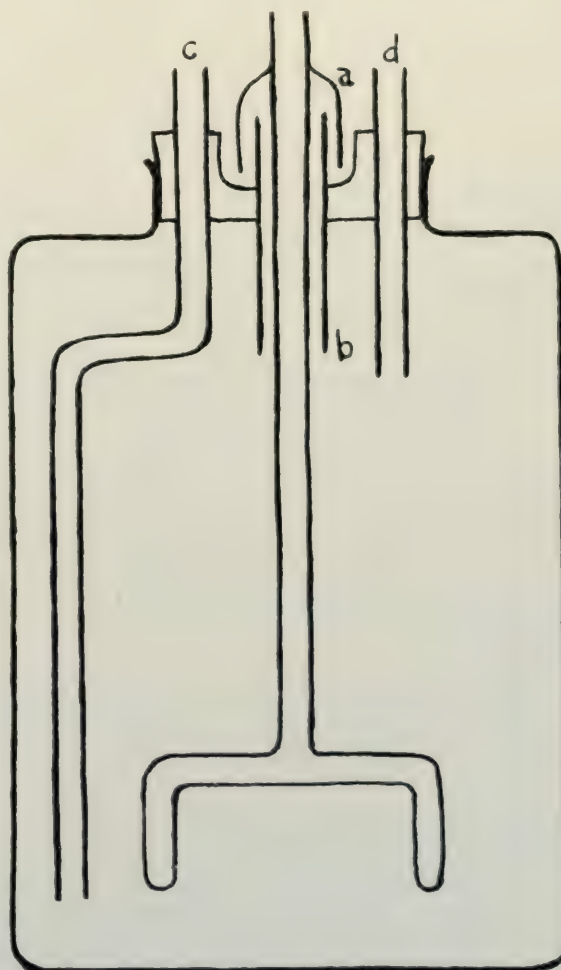
THE LOSS OF CARBON DURING SOLUTION OF STEEL IN POTASSIUM CUPRIC CHLORIDE.

By HELEN ISHAM.

Received May 22, 1911.

In a previous article⁴ the author, in collaboration with J. A. Aumer, undertook a comparison of the methods for the determination of carbon in steel by direct combustion, and by solution in acidified potassium cupric chloride solution and combustion of the residue. The results led to the conclusion that the direct combustion method afforded values averaging 0.004 per cent. higher than the solution method and that there remained in the burned steel an amount of carbon equivalent to 0.003 per cent. carbon in the original steel, making a total difference of 0.007 per cent. carbon by the two methods, a variation which might well be ascribed to experimental errors. At the same time Moore and Bain⁵ published some results on the solution method tending to show that during the solution of steel in potassium cupric chloride solution there is a loss of carbon as gaseous hydro-

carbons amounting to 0.04-0.05 per cent. in the steel, or between 7.6 and 3.4 per cent. of the total carbon. Their work consisted in dissolving 3 gram samples of steel, of 0.653 and 1.18 per cent. carbon, in potassium cupric chloride solution at 65° C., passing purified air through the solution as the reaction took place, then through a furnace, and collecting the CO₂ as BaCO₃, and determining as BaSO₄. The fact that practically the same amount of hydrocarbon gases were evolved from steel of widely varying carbon content, and the fact that comparison of the two methods carried on in this laboratory, taking into account all possible sources of error, had shown a discrepancy which at the greatest was only one-fifth as great as the loss claimed by these investigators to occur when steel is dissolved in potassium cupric chloride, has led the author to repeat that part of the work reported in the first article in which no loss of carbon was found during solution of the steel. The results have shown conclusively that an error amounting to 0.05 per cent. carbon in the steel is out of the question, that the loss is at the most less than 0.01 per cent. carbon in the steel and is in all probability to be explained by difficulties in manipulation and weighing, and that the results of Moore and Bain were in error because of gaseous carbon compounds in the potassium cupric chloride which are evolved at a



¹ J. Am. Chem. Soc., **30**, 1233 (1908).

² THIS JOURNAL, **1**, 455 (1909).

³ Chem.-Zig., **34**, 648.

⁴ J. Am. Chem. Soc., **30**, 1236 (1908).

⁵ J. Soc. Chem. Ind., **27**, 845 (1908).

faster rate when the steel is reacting with the solvent than when air is passing through the solvent alone as in the blank tests. The fact that Moore and Bain used an acidified solution of potassium cupric chloride with nothing in the chain to remove HCl carried from the solution by the current of air may account for the small amount of CO₂ found in the blank runs.

The work as performed in this laboratory has consisted in passing a current of purified air through potassium cupric chloride solution in which the steel was dissolving at room temperature and with constant stirring, then through a combustion furnace, drying it with H₂SO₄ or CaCl₂, then absorbing the CO₂ in soda lime tubes. The apparatus used consisted of a chain arranged in the following order: 1, a combustion furnace filled with CuO and heated to redness; 2, a wash bottle filled with KOH (2 : 1); 3, a special bottle in which the solution of the steel took place; 4, a second combustion furnace half filled with CuO, the last half being filled with PbCrO₄ and a coil of Ag wire; 5, a drying agent, either conc. H₂SO₄ or CaCl₂; 6, soda lime and CaCl₂ tubes for the absorption of CO₂; and 7, a safety of CaCl₂ or H₂SO₄. The bottle in which the solution took place was fitted with a cork and stirring rod as shown in the figure. The "hood" *a* on the stirring rod dipped into mercury contained in the cup formed by the stopper and the wide glass tubing *b* so that the rod could be turned rapidly in an air-tight socket. Air was passed in through *c* and out through *d*. In this way solution took place under the usual conditions of the carbon determination, namely with rapid stirring and at room temperature.

Table I is the result of some preliminary work carried on by A. R. Pollard and is of interest in that it furnishes a possible explanation of the results found by Moore and Bain. The column "per cent. loss of carbon from steel" was obtained by subtracting from the weight of CO₂ the average weight of CO₂ obtained from the blank determinations, then calculating to carbon. The first potassium cupric chloride solution, "soln. A," had been made up for some time and gave blanks as indicated, but when it became necessary

to make up a new solution, "soln. B," the first blank on that solution gave a very large gain in weight and it was only after air had been passed through the solution for 24 hours that the blanks recorded were obtained. The results indicate a loss of carbon of the same order as that reported by Moore and Bain.

Table II shows the results of dissolving steel in acidified potassium cupric chloride solution which is free from gaseous carbon compounds. The solution was made according to the proportions given by Dudley,¹ one pound of crystallized salt being dissolved in 1.3 l. of water and, after air had been blown through the solution for three to four days, 100 cc. conc. HCl added. It was found necessary to continue blowing air through the solution for as much as three days to completely remove the carbon gases, the identification of which has not been attempted. In all cases, those in which no steel was dissolved as well as the others, the solution was stirred vigorously and continuously at about 25° C. In the cases where steel was dissolved the solution was complete in the time specified. The absorption tubes were weighed against tares which were given the same treatment as the tubes except that they were not connected with the chain during a determination.

TABLE II.

No.	K ₂ CuCl ₄ soln.	Nature and weight of steel.	Per cent. carbon in steel.	Change in wt. of soda lime tubes, Gram.	Duration of run, Hrs.
1	200 cc. C		+0.0011	2
2	200 cc. C		+0.0004	2
3	200 cc. C	Bessemer, 5 grams	0.206	+0.0002	3
4	200 cc. C		-0.0007	1 1/2
5	200 cc. C	Bessemer, 5 grams	0.441	+0.0007	2
6	200 cc. C	Basic open hearth, 5 grams	0.834	+0.0001	3
7	200 cc. C	Basic open hearth, 5 grams	1.048	-0.0006	2
8	200 cc. D		+0.0003	1 1/2
9	200 cc. D	Basic open hearth, 5 grams	1.048	-0.0002	2
10	200 cc. D		+0.0003	3
11	200 cc. D	Bessemer, 5 grams	0.441	-0.0005	2 1/2
12	200 cc. D	Iron C, 5 grams	3.26	-0.0004	2
13	200 cc. D	Iron A, 5 grams	3.67	+0.0001	2

After the first blank, showing a gain of 0.0011 gram in the weight of the soda lime tubes, air was passed through the solution for 12 hours and a second blank determination made which was considered within the limits of accuracy of weighing. The greatest difference between a blank and solution is found in experiments Nos. 4 and 5, and the total difference, 0.0014 gram CO₂, amounts to 0.008 per cent. carbon in the steel. In all other cases the difference between the blank and the solution varies between +0.0008 and -0.0008 gram, the average change in weight of the soda lime in blank runs (omitting No. 1) being +0.0001 and in the determinations in which solution was taking place -0.0001, a result which seems clearly to indicate that there is no evolution of gaseous hydrocarbons during the solution of steel in potassium cupric chloride.

Between Nos. 7 and 8, Table II, the H₂SO₄ (No. 5 in the chain) was replaced by CaCl₂ which had been

TABLE I.

No.	K ₂ CuCl ₄ soln.	Nature ¹ and weight of steel.	Per cent. carbon in steel.	Gain in weight of KOH due to CO ₂ Gram.	Per cent. loss of carbon from steel.
1	200 cc. A		0.0045
2	200 cc. A		0.0046
3	200 cc. A		0.0050
4	200 cc. A	Bessemer, 5 grams	0.203	0.0100	0.029
5	200 cc. A	Bessemer, 5 grams	0.203	0.0090	0.023
6	200 cc. A	Bessemer, 3 grams	0.203	0.0080	0.030
7	200 cc. A	Bessemer, 3 grams	0.203	0.0080	0.030
8	200 cc. B		0.0032
9	200 cc. B		0.0037
10	200 cc. B		0.0035
11	200 cc. B	Basic open hearth, 3 grams	1.048	0.0070	0.033
12	200 cc. B	Basic open hearth, 3 grams	1.048	0.0073	0.035
13	200 cc. B	Basic open hearth, 3 grams	0.608	0.0060	0.024
14	200 cc. B	Basic open hearth, 3 grams	0.608	0.0062	0.025

¹ The iron and steel samples used were those prepared by the Bureau of Standards, and the carbon content given is the average reported by the Bureau of Standards.

¹ J. Am. Chem. Soc., 15, 533 (1893).

saturated with CO_2 . The two iron samples, Nos. 12 and 13 have total carbon as shown in the table; iron C has 0.58 per cent. and iron A 0.77 per cent. combined carbon.

The results obtained have been so entirely uniform that it was deemed unnecessary to continue the work further, and the conclusion reached is that the apparent loss of carbon during solution of steel in potassium cupric chloride at ordinary temperatures is due to gaseous carbon compounds present in the reagent and not to the formation of such from the carbon in the steel. There is no appreciable loss of carbon from the steel.

In the previous article the authors promised further work on the determination of sulphur by direct combustion of steel and evolution of sulphur dioxide and trioxide. All efforts to bring the process to a satisfactory method for the determination of sulphur have failed, because, apparently, the sulphur will not burn out completely from so large an excess of iron.

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CONTRIBUTIONS TO THE CHEMISTRY OF ANAESTHETICS, III: NITROUS OXIDE.¹

By CHARLES BASKERVILLE AND RESTON STEVENSON.

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One of the first outcomes of the establishment of the Pneumatic Institute may be given in the historical sentence of Davy, who breathed "dephlogisticated nitrous air" (nitrous oxide), recorded his sensations and the behavior of others after the inhalation: "As nitrous oxide in its extensive operation appears capable of destroying physical pain, it may probably be used to advantage during surgical operations in which no great effusion of blood takes place."² In 1844, Drs. Colton and Wells demonstrated this use in dental surgery. It is now used extensively, alone or with other anaesthetics, in general surgery.

This communication records the results of an examination of commercial nitrous oxide, supplied on the American market for anaesthetic purposes, and it presents a new method for the quantitative determination of nitrous oxide.

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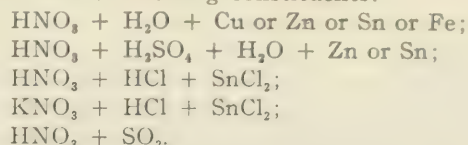
(a) Preparation.

1. *Heating NH_4NO_3 .*—In 1793, Deimann, von Troostwyer, Nieuwland, Bont and Louwerburgh

prepared N_2O by heating NH_4NO_3 , and in 1800 Davy¹ published his researches upon this gas. Others² have determined, for the decomposition of NH_4NO_3 by heat, the best conditions, such as apparatus, temperature, pressure, moisture, acidity, physical structure, and catalytics. Pelouze³ prepared N_2O by heating $\text{NH}_4\text{NO}_3 + \text{H}_2\text{SO}_4$ to 150° .

2. *Heating Mixed Salts.*—To prevent the explosive formation of N_2O , and to employ cheaper constituents, Watson Smith⁴ and others⁵ have used the following mixed salts: $\text{KNO}_3 + \text{NH}_4\text{Cl}$; $\text{NaNO}_3 + \text{NH}_4\text{Cl}$; $\text{Pb}(\text{NO}_3)_2 + (\text{NH}_4)_2\text{SO}_4$; $\text{NaNO}_3 + (\text{NH}_4)_2\text{C}_2\text{O}_4$; $\text{NaNO}_3 + (\text{NH}_4)_3\text{PO}_4$; $2\text{NaNO}_3 + (\text{NH}_4)_2\text{SO}_4$ (especially). N_2O may also be prepared by the decomposition of ammonium nitrosulphate by hot water⁶ or by heating NH_4Cl with dilute HNO_3 to 100° .⁷

3. *Reduction of HNO_3 and of Nitrates.*—In 1776, Priestley obtained N_2O by reduction of dilute HNO_3 by metals. Others⁸ have shown that it may be made by reaction of the following constituents:



It is also found⁹ when milk putrefies in the presence of nitrates.

4. *Reduction of HNO_2 and of Nitrites.*— HNO_2 and nitrites in acid solutions are reduced to N_2O by the following reagents: H_2SO_3 ,¹⁰ hydroxylamine sulphate,¹¹ $\text{Fe}(\text{OH})_2$,¹² sodium amalgam,¹³ or $\text{Na}_2\text{S}_2\text{O}_3$.¹⁴

5. *Reduction of NO .*—In 1772, Priestley discovered N_2O by reducing NO by moist iron.¹⁵ NO has also been reduced to N_2O by Gay-Lussac and others¹⁶ by the following reagents: H_2S , sulphides, Zn, FeSO_4 , SO_2 , sulphites, SnCl_2 , and NH_3 .

6. *Oxidation of Hydroxylamine.*¹⁷—Hydroxylamine and its salts are oxidized with the formation of N_2O

¹ Loc. cit.

² Hare, *Am. J. Sci.*, **16**, 295 (1829); Porter, *Pharm. J.*, **11**, 62 (1869); Veeley, *J. Chem. Soc.*, August, 1883; *Phil. Trans.*, **1885**, 257; Cazeneuve, *J. Pharm. Chim.*, [5], **11**, 67; Thilo, *Chem.-Ztg.*, **18**, 532; U. S. Dispensatory, 1899; Lidoff, *J. Russ. Phys.-Chem. Soc.*, **35**, 59 (1903).

³ *Compt. rend.*, **12**, 599 (1841).

⁴ W. Smith and W. Elmore, Eng. Pat. 9,023, 1891; W. Smith, *J. Soc. Chem. Ind.*, **11**, 867 (1892); W. Smith, *Ibid.*, **12**, 10 (1893).

⁵ Gronvelle, *Ann. chim. phys.*, **17**, 351; Pleischel, *Schw. J.*, **38**, 461; Soubeiran, *Ann.*, **23**, 59 (1838).

⁶ W. Smith, *J. Soc. Chem. Ind.*, **1892**, 867.

⁷ J. L. Smith, *Am. J. Sci.*, [2], **15**, 240 (1852).

⁸ Gay-Lussac, *Ann. chim. phys.*, [3], **23**, 229 (1848); Millon, *J. Pharm. Chim.*, **29**, 179; Schiff, *Ann.*, **113**, 84 (1862); Fr. Mareck, *Jahresber.*, **1885**, 355; Basset, *Chem. News*, **53**, 172 (1886); Compari, *Compt. rend.*, **1888**, 1569.

⁹ Schlössing, *Compt. rend.*, **66**, 237.

¹⁰ Rudweber, *Chem. Centr.*, **38**, 22 (1867); Fremy, *Compt. rend.*, **70**, 61 (1870).

¹¹ Meyer, *Ann.*, **174**, 141 (1875); Guye and Bogdan, *Compt. rend.*, **138**, 1494 (1904).

¹² Dumreicher, *Wien Akad. Ber.*, **82**, 560 (1880).

¹³ Zorn, *Ber.*, **15**, 1258 (1882).

¹⁴ Meyer, *Z. anorg. Chem.*, **34**, 49 (1903).

¹⁵ See Priestley's "Experiments and Observations on Different Kinds of Air," Vol. I, p. 3. "Memoirs of Joseph Priestley to the Year 1795," 1803, 1.

¹⁶ Gay-Lussac, *Ann. chim. phys.*, **1**, 394 (1816); Schiff, *Ann.*, **113**, 84 (1862); Kuhlmann, *Poly. J.*, **211**, 24 (1874); Gray, *Compt. rend.*, **89**, 410 (1879); Pelouze, *Ann. chim. phys.*, **60**, 162.

¹⁷ V. Meyer, *Ann.*, **174**, 141 (1875); Donath, *Wien Akad. Ber.*, **75**, 566 (1877); Guye and Bogdan, *Compt. rend.*, **138**, 1494 (1904).

¹ Read before the New York Section, May, 1911.

² Davy, "Researches Chemical and Philosophical, Chiefly Concerning Nitrous Oxide or Dephlogisticated Nitrous Air, and Its Respiration," London, 1800.

by the following substances: NaNO_2 , alkaline cupric solution, $\text{Fe}_2(\text{SO}_4)_3$, iodine, and AgNO_3 .

7. *From the Air*.—It is claimed that air can be oxidized to N_2O in a tube heated either electrically¹ or by an oxyacetylene flame;² and it is claimed that in the presence of H_2 or NH_3 and an oxidizable metal (Cu, Fe, etc.), air, upon heating, forms N_2O , etc.³

(b) *Method of Analysis*.

1. *Decomposition into $\text{N}_2 + \text{O}_2$* .—Priestley decomposed N_2O into $\text{N}_2 + \text{O}_2$ by heat, and after him, others,⁴ using, as sources of heat, gas-heated capillary Pt tube, electrically heated Pt wire, gas-heated porcelain tube, gas-heated Pt and Pd asbestos, silent electric discharge, or spark discharge. In all of these methods, however, it is claimed⁵ that other oxides of nitrogen are formed.

2. *Burning with Hydrogen*.—Winkler⁶ and others recommended the determination of N_2O by burning it with H_2 in a capillary Pt tube, etc. The reliability of this method has been questioned,⁷ because of incomplete combustion and the formation of other oxides of nitrogen.

3. *Explosion with Hydrogen*.—Bunsen⁸ used this method to determine N_2O , and after him others⁹ decided the proper conditions for the best results. Hydrogen should be present to the extent of 2 or 3 times the volume of N_2O and the presence also of oxygen is recommended. The accuracy of this method has been questioned,¹⁰ because of the formation of other oxides of nitrogen.

4. *Various Methods*.—These various methods have been recommended for the determination of N_2O : passing over ignited charcoal and absorption of the CO_2 ;¹¹ explosion with CO ;¹² decomposition by electrically heated iron spiral;¹³ passing over fused $\text{Na}_2\text{CO}_3 + \text{Cr}_2\text{O}_3$ and titration of the Na_2CrO_4 formed;¹⁴ absorption in alcohol.¹⁵

(c) *Purification*.

Commercial N_2O is apt to contain these impurities: Cl_2 , NO , NO_2 , HNO_3 , NH_3 , HCl , CO_2 , O_2 , N_2 , and rare gases of the air. It is purified by passage through solutions of NaOH , FeSO_4 , and H_2SO_4 . Further purification is accomplished by the formation of a

hydrate¹ below 0°C . and heating this hydrate; by fractional condensation;² and by fractional distillation.

B. EXPERIMENTATION.

(a) *Methods of Analysis Used*.

The following impurities may be suspected in a cylinder of nitrous oxide gas:

1. Solids;
2. Liquids;
3. Gases and Vapors:
 - H_2O ;
 - Halogen Acids, HNO_3 , Organic Acids;
 - O_3 , NO_2 , N_2O_3 , SO_2 ;
 - NH_3 , Organic Bases;
 - CO_2 , Halogens, Oxides of Chlorine;
 - HCN , $(\text{CN})_2$;
 - PH_3 , SbH_3 , AsH_3 , H_2S ;
 - O_2 , H_2 , NO ;
 - CO , CH_4 , Organic Matter;
 - N_2 , Rare Gases of the Air.

For these impurities, a qualitative search was first made and then, whenever necessary, a quantitative determination. The following systematic procedure was used.

Experiment 1.

Train:

- Cylinder;
- Trap + litmus + starch-KI papers;
- P_2O_5 U-tubes (1) and (2);
- CaCl_2 guard tube;
- Moistener + litmus + starch-KI papers;
- $\text{Ba}(\text{OH})_2$ Aq (1);
- $\text{Na}(\text{OH})$ Aq;
- AgNO_3 Aq;
- Alk. Pyrogallol Aq;
- 2 CaCl_2 tubes;
- CuO furnace;
- CaCl_2 U-tubes (1) and (2);
- $\text{Ba}(\text{OH})_2$ Aq (2);
- NaOH tube;
- Gasometer.

By this experiment, any solids and liquids were caught in the trap and by the litmus and starch-KI papers tested for acids, bases, halogens and ozone. The moisture was determined quantitatively by the weighed U-tube containing P_2O_5 on glass wool and the accuracy of this determination checked by the second weighed P_2O_5 U-tube. The CaCl_2 protected the P_2O_5 tube from absorption of water from the moistener. This apparatus is the same as that used in the examination of oxygen and is shown in Fig. 13 in that communication; the gas enters at A, it then passes the wet porous cotton rope B which does not contain enough water to absorb the impurities from the gas, but moistens it enough to enable the impurities in it to react with test papers, and then the gas passes through cones C, D, E, of blue and red litmus and starch-KI papers, repeating the tests made before in the trap tube. The

¹ Villard, *Compt. rend.*, **118**, 1096 (1894).

² Erdmann und Stolzenberg, *Ber.*, **43**, 1702 (1910); Stolzenberg, *Ibid.*, **43**, 1708.

³ THIS JOURNAL, July, 1911, p. 474.

¹ Södermann, French Pat., 411,785, 1910.

² Pictet, French Pat., 415,594, 1910.

³ Marston, Eng. Pat., 19,074, 1900.

⁴ Berthelot, *Compt. rend.*, **77**, 1448 (1874); *Bull. soc. chim.*, [2], **26**, 101 (1876); *Compt. rend.*, **82**, 1360 (1876); Winkler, *Untersuchung der Industrie Gase*, 1877; Graham-Otto, *Lehrbuch der Chemie*; Lunge, *Ber.*, **14**, 2188; Kemp, *Chem. News*, **71**, 108 (1895).

⁵ *Ibid.*

⁶ Winkler, *Untersuchung der Industrie Gase*, 1877; Montmartini, *Atti Accad. Lincei*, **7**, II, 219 (1893); Classen, *Angewählte Methoden*, 1903.

⁷ Lunge, *Ber.*, **14**, 2188; Kemp, *Chem. News*, **71**, 108 (1895).

⁸ Bunsen, *Gas analytische Methoden*, 1877.

⁹ Winkler, *Untersuchung der Industrie Gase*, 1877; Dumreicher, *Wien Akad. Ber.*, **82**, 560 (1880); Hempel, *Ber.*, **15**, 903 (1882).

¹⁰ Lunge, *Ber.*, **14**, 2188.

¹¹ Winkler, *Untersuchung der Industrie Gase*, 1877.

¹² Kemp, *Chem. News*, **71**, 108 (1895).

¹³ Guye and Bogdan, *Compt. rend.*, **139**, 1494 (1904); Jacquerod and Bogdan, *Compt. rend.*, **139**, 49 (1904); Buff and Hoffman, *Ann.*, **113**, 129.

¹⁴ Wagner, *Z. analyt. Chem.*, **21**, 374 (1882); Crookes, *Select Methods in Chem. Anal.*, 1905.

¹⁵ Carius, *Chem. Centr.*, **26**, 433 (1885); Lunge, *Ber.*, **14**, 2188 (1881).

nearly saturated $\text{Ba}(\text{OH})_2\text{Aq}$ showed the presence or absence of CO_2 , and after the run this solution was divided into three portions: the first portion acidified with HCl gave a test for SO_3 ; the second portion with $\text{HNO}_3 + \text{AgNO}_3$ for halogens, halogen acids, and halogen oxides; and the third portion was set aside. After the run, the NaOHAq (2 : 3) was divided into three portions; to the first portion was added BaCl_2 and then HCl in excess, thus testing for CO_2 , SO_2 , SO_3 ; the second portion was acidified with HNO_3 , then made ammoniacal and AgNO_3 added, and finally acidified with HNO_3 , thus testing for SO_2 , H_2S , halogens, halogen acids, and halogen oxides; the third portion was mixed with the third portion of the $\text{Ba}(\text{OH})_2\text{Aq}$, and tested for HCN and $(\text{CN})_2$ by boiling with $\text{Fe}(\text{OH})_2 + \text{Fe}(\text{OH})_3$ and acidifying with HCl to form Prussian blue. The AgNO_3Aq repeats some of the previous tests and in addition shows the absence or presence of PH_3 , SbH_3 , and AsH_3 . The gas is tested for O_2 by the darkening of the alkaline pyrogallol Aq ; then it is dried by the two CaCl_2 tubes and the H_2 and organic compounds are oxidized by the red-hot CuO . The water which is formed is weighed in the CaCl_2 U-tube (1) which is guarded by the weighed CaCl_2 U-tube (2); and the CO_2 which is formed gives a precipitate in the nearly saturated $\text{Ba}(\text{OH})_2\text{Aq}$ (2). This last solution is guarded by a tube containing solid NaOH . The gas is measured in the gasometer. From 10 to 18 liters of gas are usually passed in from 3 to 6 hours; the separate bubbles could easily be counted.

Experiment 2.

Train:

Cylinder;
Trap + litmus and starch-KI papers;
 FeSO_4Aq ;
 KMnO_4Aq ;
 $\text{CuCl} + \text{HCl} + \text{Aq} + \text{PdCl}_2$;
 NaOH sol. ;
Gasometer.

The trap and test papers used in Experiment 1 were again used in this experiment, so that the tests were repeated in an accumulative manner. The slightly acid solution of FeSO_4 tests for NO , and its titration after the run showed the presence or absence of active oxidizing agents—although O_2 would not have affected it.¹ The KMnO_4Aq , made by adding one drop of $N/2$ KMnO_4 to 500 cc. H_2O , tests for reducing agents. The solution of PdCl_2 in an HCl solution of CuCl was diluted with H_2O after each run as a test for CO .² The NaOH solution absorbed any HCl from the previous solution before the gas was measured in the gasometer.

In addition to these qualitative determinations, confirmatory tests were made for chlorine by AgNO_3 and for hydrogen by anhydrous CuSO_4 placed after the combustion furnace.

Experiment 3.—Alkaline pyrogallol showed in each instance no certain absorption of the gas, indicating the absence of oxygen and CO_2 in amounts greater than a trace.

Experiment 4.— NH_3 was determined quantitatively by passing the gas slowly through water to which

Nessler's reagent had been added, and comparing the color developed with the ammonia standards such as are used ordinarily in water analysis.

Experiment 5.—It was attempted to determine the N_2O by absorption at 0° in absolute alcohol which had been boiled free from gases. In every instance the gas was practically completely absorbed irrespective of the amount of impurities present. For independent accurate determination, therefore, this method is untrustworthy. Under standardized conditions, however, it might be used as an approximate method for works analysis or factory control.

Experiment 6.—The gas was exploded with about 3 times its volume of hydrogen and the contraction in volume noted—a determination according to Bunsen's method.¹ The duplicate results agree but there is a constant divergence from the true percentage of about—2 per cent. (see *comparison of results*). This method was used by Smith and Leman.² It came to our notice in reading the proof.

Experiment 7.—Because of the lack of a reliable method for the accurate determination of N_2O , the authors have devised and tried the following method: Hydrogen was passed over ignited copper in a combustion tube until complete reduction; then the tube was allowed to cool while the stream of hydrogen continued. When cold, the hydrogen was replaced by CO_2 , the tube was reheated and the gas sample passed over the Cu , oxidizing it to CuO . The hydrogen was passed until complete reduction and until the moisture was swept out of the tube. The H_2O which was formed was caught in a weighed CaCl_2 tube.

This method gave excellent results, but it was simplified and improved as in the following experiment.

Experiment 8.— N_2O was determined by passing the sample of gas over reduced copper in an atmosphere of hydrogen, then reducing the CuO by a stream of hydrogen and collecting the H_2O which was formed in a CaCl_2 tube.

In detail, the method is as follows: Hydrogen from a Kipp generator containing zinc and H_2SO_4 (1 : 6), to which 2 drops of $\text{H}_2\text{PtCl}_6\text{Aq}$ have been added, passes through a tower of solid NaOH and a long CaCl_2 tube to a hard glass combustion tube. This tube rests upon asbestos in an iron trough heated in a combustion furnace to a dull red color; it is 100 cm. long and contains snugly-fitting rolls of copper gauze aggregating 70 cm. in length. The farther end of this tube is drawn out to a narrow bore, which is inserted into a CaCl_2 tube and joined with rubber. This CaCl_2 tube is joined to a second similar tube and thence connected with a test tube containing any liquid to show the rate of passage of the gas.

The hydrogen is passed until the copper is completely reduced and the two CaCl_2 tubes have reached a constant temperature. Then it is stopped and about 800 cc. of the gas sample of accurately measured volume, temperature, and pressure, are passed through the tube at the rate of about 2 bubbles per second. This requires about 1 hour. The farthest rolls of gauze (about 15 cm.) should not be, and in our

¹ *J. Am. Chem. Soc.*, July, 1911.

² Hempel's "Gas Analysis," trans. by Dennis, 1906, p. 210.

¹ Hempel's "Gas Analysis," trans. by Dennis, 1906, p. 198.

² *J. Am. Chem. Soc.*, 33, 1114, 1911.

experiments were never, oxidized. Hydrogen is then passed through at the rate of 3 or 4 bubbles per second until all of the CuO is reduced and all of the moisture driven out of the tube into the CaCl_2 tubes, this process requiring about $\frac{3}{4}$ hour. The combustion tube and the CaCl_2 tubes are then ready for a second determination, to begin with the passage through the tube of the sample of nitrous oxide.

About 2 hours are required for each determination, if many are made consecutively; a single determination made alone would require about 3 hours.

The usual precautions were taken to prevent any leaking of gas, and a trap was used to catch any mercury and prevent its getting into the combustion tube. In our experiments, the second CaCl_2 tube remained almost constant, gaining about 1 mg. in weight each time. If as much as a liter of gas is taken as a sample and its volume, temperature, and pressure carefully measured, this method probably would yield results sufficiently accurate for an atomic weight determination. Of course, since this is a determination of the N_2O indirectly by the direct determination of the oxygen present, therefore the H_2O from other oxygen compounds and also the moisture present in gas must be subtracted.

(b) Results and Conclusions.

The following table, which is self-explanatory, exhibits the results of our analyses of compressed nitrous oxide as supplied by American manufacturers:

Analysis									
No.	N_2O	H_2O	CO_2	NH_3	O_2	N_2 , etc., by difference.	N_2O by explosion.	N_2O by $\text{Cu} + \text{CO}_2 + \text{H}_2$	N_2O by $\text{Cu} + \text{H}_2$
1	99.7	0.13	0	0.006	present	0.16	97.5	99.4	99.7
2	96.6	0.15	0	0.001	present	3.25	95.0	96.2	96.6
3	99.5	0.15	0	0	present	0.35	97.3	99.5	99.5
4	95.9	0.16	present	0	present	3.94	94.1	95.6	95.9

C. RECOMMENDATIONS.

Nitrous oxide which is to be used for anaesthetic purposes should contain at least 95 per cent. of N_2O and no solids, liquids, combustible organic matter, chlorine, or other oxides of nitrogen. The last two impurities may be tested for by slowly passing 10 liters (3 hours) through silver nitrate and ferrous sulphate solutions.

COLLEGE OF THE CITY OF NEW YORK.

[FROM THE RESEARCH LABORATORY OF PARKE, DAVIS & CO., DETROIT, MICH.]

SOAPS FROM DIFFERENT GLYCERIDES.—THEIR GERMICIDAL AND INSECTICIDAL VALUES ALONE AND ASSOCIATED WITH ACTIVE AGENTS.

By H. C. HAMILTON.

Received Apr. 1, 1911.

The paper herewith presented is largely characterized by its biological features. It has, however,

¹ Lack of knowledge of the content of real N_2O may seriously interfere with the satisfactory use of this, the safest, anaesthetic, especially when it is administered by the proper method, namely, mixed with oxygen. If the preparation contains more than 95 per cent. N_2O , the variation in the proportion of the two gases will depend then, in fact, upon the amount of oxygen actually mixed and the percentage is not seriously altered (Gwathmey and Baskerville).

certain points of a strictly chemical nature. It is therefore presented with the hope of arousing an interest in the chemistry of insecticides and germicides, a subject which has received comparatively little consideration.

In a paper¹ presented before the International Congress of Zoologists in 1907, the writer stated: "We have confirmed the fact that the insecticidal value of soap is very considerable. This might raise the question whether the average coal tar dip on the market, the efficient dilution of which in most cases is not greater than one in seventy-five, does not owe a large part of its efficiency to the soap contained." It is a matter of fact that the average soap is more strongly insecticidal than the average coal tar dip since the bed-bug is killed in most cases by being submerged for one minute in a 1 per cent. solution of soap while few coal tar dips will kill this insect under the same conditions, unless a solution is used one and a half to two times as strong. In spite of this, soap is looked upon merely as a convenient and valuable solvent for other substances which are classed as insecticides or germicides.

When we consider, on the other hand, the germicidal value of soaps, no such high value is inherent in them. They require the addition of an alkali or an antiseptic agent to give them even a nominal value.

As solvents of germicides, however, soaps have in some instances an efficiency greatly out of proportion to their apparent value. For instance, a mixture of carbolic acid and soap, equal parts, has the same germicidal value when diluted 1-75 as the carbolic acid alone, diluted with water 1-100. The quantity of carbolic acid in the soap mixture is such as to give an actual dilution of 1-150, an increase of 50 per cent. in its germicidal value due to the addition of soap.

Tests to determine the germicidal value of the soap alone indicate that the quantity present could not in itself have exerted any action whatever.

The writer recently had occasion to prepare a disinfectant which differed from the common commercial product, in that certain ingredients were added to overcome the disagreeable odor. At the same time the attempt was made to retain the germicidal value with a material reduction in its cost.

One method by which it was planned to accomplish the latter purpose was by the use of a cheaper saponifiable oil. The preliminary work had been done, using linseed oil soap; the physical properties and germicidal values were satisfactory and a formula was worked out. In this formula cottonseed oil was substituted for the more expensive linseed, with no impairment in the physical properties of the resultant product. The germicidal test, however, showed a marked lowering in the value of the product so prepared.

By a process of exclusion the cause of this was finally located in the oil used in making the soap, and a series of tests was carried out to see if any

¹ "A Contribution to Our Knowledge of Insecticides."

considerable difference could be detected in the germicidal values of soaps from the different glycerides or whether the difference was apparent only when the soap and an active agent were used in combination.

Table I shows the comparative values of two disinfectants differing in composition only in the oil used for making the soap. Disinfectant A contains linseed oil soap; disinfectant B, cottonseed oil soap.

TABLE I.

	Dilution.	Time in minutes.				
		1.	2.	3.	4.	5.
A.....	1-200	+	—	—	—	—
	1-250	+	+	—	—	—
	1-300	+	+	+	+	—
B.....	1-200	+	+	+	+	—
	1-250	+	+	+	+	+
	1-300	+	+	+	+	+

In these tables + stands for growth of organism, — stands for no growth. The organism is grown in bouillon and the culture used is a 24-hour growth of *B. typhosus*. In making the test the culture is thoroughly shaken and filtered through cotton, in order to remove clumps of bacteria which might interfere with the test. The disinfectant is diluted as shown in the table, 1 part in 200, 250 and 300, using about 5 cc. of the diluted disinfectant and 5 drops of the culture, dropped from a standard pipette, which delivers approximately $\frac{1}{20}$ of a cubic centimeter. After mixing the bacteria with the germicide they are allowed to remain in contact for 1 minute, at the end of which time a loop full of the mixture of bacteria and disinfectant is planted in a tube of sterile bouillon and placed in the incubator for 48 hours. This is repeated at the end of two minutes, three minutes, four minutes, and five minutes. The results, therefore, represent the action of the germicide on the naked bacteria.¹ The object in filtering the bacteria to remove any masses is to obtain the actual germicidal value and not the penetrating value of the product, two properties which are entirely distinct. This method is practically that called the Rideal-Walker method, which is official in Great Britain as a means of standardizing disinfectants.

An article which appeared in the *Medizinische Klinik*, 1910, No. 36, "Concerning the Disinfectant Constituents of Soap," threw no light on this question except in so far as this value is connected with the saturated fatty acids. It was claimed that a soap from palmitic acid or a tripalmitate had antiseptic value in itself greater than that of carbolic acid. A series of experiments was carried out to see if the soaps of the different glycerides differed among themselves in germicidal value.

The following table, Table II, shows the results obtained from a series of tests using *B. typhosus* as the test organism and carried out in a way practically identical with the Rideal-Walker method than which probably not better has yet been found:

¹ The germicidal tests were in all cases carried out at approximately 20° C.

TABLE II.

Glyceride.	Oil used.	Dilution.	Result in 5 min.
Trilaurin	Cocoonut	1-40	—
		1-50	+
Tribrassin	Rape seed.....	1-20	+
Trivalerin	Whale.....	1-20	+
Trilinolein	Linseed.....	1-20	+
Tricicnolein	Castor.....	1-40	—
		1-30	+
Tripalmitin	Palm.....	1-20	+
Triolein	Olive.....	1-20	—
		1-30	+
	Resin.....	1-20	+

Insecticidal tests, Table III, were also carried out using the common bed-bug, *Cimex lectularius*, as the experimental organism and following the method described in the paper to which reference was made in the opening paragraph.

The method may be briefly described as follows: The insects are placed in tubes open at both ends, and imprisoned by covering the ends with a porous cloth (India mull). Then by using a hook which will fasten into the cloth, the tube with the insects is quickly plunged into the solution. By rapid agitation, the protective air globules which surround the spiracles can be removed so that intimate contact with the insecticide results. At the end of the period of time, usually one minute, during which time the insect is submerged, it is quickly removed with the hook and the clinging solution shaken off, the capillary action of the cloth tending to draw off all excessive moisture.

It is then transferred to bibulous paper and covered with a clock glass, which allows sufficient air and easy observation.

TABLE III

Glyceride.	Represented by:	Dilutions.			
		50.	100.	200.	300.
Trilaurin	Cocoonut oil	dead	3 dead 1 alive	3 alive 1 dead	alive
Tribrassin	Rape seed oil	dead	alive	alive	alive
Trivalerin	Whale oil	dead	dead	2 alive 2 dead	alive
Trilinolein	Linseed oil	dead	dead	2 alive 2 dead	alive
Tricicnolein	Castor oil	dead	dead	2 alive 2 dead	alive
Tripalmitin	Palm oil	dead	dead	3 alive 1 dead	alive
Triolein	Olive oil	dead	dead	3 alive 1 dead	alive
	Resin oil	dead	2 dead 2 alive	4 alive	alive

These soaps were dissolved in 50% alcohol, so that a certain weight of soap was contained in a definite volume of alcohol, in most cases 1 gram of soap in 3 cc. alcoholic solution.

A study of Table II shows that cocoonut oil soap has the highest value as a germicide. Castor oil and olive oil were the only others tested which had germicidal action in 5 per cent. solution, the others scarcely showing even an inhibiting action on the growth in bouillon.

The insecticidal values indicate that no considerable difference exists in the potassium soaps of the different glycerides, a 1 per cent. solution being efficient

in every case but one—that of the soap from rape seed oil. The same soaps mixed with active agents, namely, a rather high-boiling tar acid and a solution of caustic potash, had entirely different effects on the germicidal values from what one would expect. The extended tests on these lines were carried out using only two of the glycerides, trilaurin and triolein, as represented by coconut oil and olive oil, because these showed wide variation in their germicidal values without added ingredients and because of the limited time to complete the tests.

Table IV, here shown, is a compilation of the results obtained from tests of these two soaps used:

First, alone.

Second, with cresylic acid.

Third, with alkali (KOH).

Fourth, with both.

Tests were also made for the value of the alkali alone, and of the alkali and cresylic acid together.

The columns headed "Coefficients," Table IV, show the number of times the preparation can be diluted compared with carbolic acid, and retain an equal efficiency.

TABLE IV.
Olive Oil Soap.
Effective dilution. Coefficients.

Combination.	Germi- cidal.	Insecti- cidal.	Germi- cidal.	Insecti- cidal.
Soap alone.....	1-20	1-100	0.17	5.0
Soap and cresylic acid...	1-500	1-300	4.0	15.0
Soap and alkali.....	1-1100	1-50	9.0	2.5
Soap, cresylic acid, and alkali.....	1-1000	1-300	8.3	5.0
Coconut Oil Soap.				
Soap alone.....	1-40	1-100	0.33	5.0
Soap and cresylic acid..	1-1000	1-100	8.3	5.0
Soap and alkali.....	1-1100	1-200	9.0	10.0
Soap, cresylic acid, and alkali.....	1-1000	1-300	8.3	15.0
Cresylic acid and alkali.	1-400	1-25	3.3	1.25
Alkali (KOH) alone.....	1-1200	1-25	10.0	1.25

In every mixture above described the ingredients are present in equal proportions and in every case the dilutions given are for each ingredient.

The literature on this subject is very contradictory. Some investigators claim that the soap constituents in themselves are valuable and that no difference exists between those from different glycerides. Most of the authors consulted conclude that alkali, volatile oils, or other germicidal agents must be present to give a perceptible value.

Rosenau¹ makes the following statement: "Medicated soaps are for the most part a snare and a delusion so far as any increased germicidal action is concerned; in fact, the addition of carbolic acid and other substances, which have the property of combining with the soap, seems actually to diminish the disinfecting power of that substance."

It should be noted in this connection that without the closest attention to the preparation of the soap, variable results are to be expected. In fact, variations were observed for which no logical reason could be deduced. It is probable that a rigid chemical control of the reactions involved would throw consid-

erable light on the subject and explain many of the discrepancies which now appear to make the literature untrustworthy.

One point should be noted, that bacteriologists have not used the same organism in making their tests. It is a well known fact that bacteria differ greatly in their resistance toward germicides, *B. typhosus* being killed by some germicides in a dilution 4 to 5 times as high as that required to kill *B. pyocyaneus*.

Another point of importance is the effect of hydrolysis on the germicidal value of the soap solution.

The table (Table V) here given is for comparison of the values of a dilution when freshly made and again after 18 hours standing.

TABLE V.

Olive oil soap and cresylic..	1-300	—	—	—	—
Same after 18 hours.....	1-300	+	+	+	—

This shows an evident deterioration probably on account of chemical changes in the solution.

SUMMARY AND CONCLUSIONS.

1. *B. typhosus* is especially susceptible to the germicidal action of alkali (KOH).

2. The combination of soap with an active agent does not invariably enhance the germicidal value of the latter.

3. The germicidal value of the combination of soap and cresylic acid depends on the glyceride used in the manufacture of the soap. One may therefore conclude that the soap exerts a distinct influence on the value of this agent.

4. The germicidal value of the alkali is not increased by any combination used in this series of tests. When combined with cresylic acid, its value is one-third that of the alkali alone.

5. With our present knowledge of the chemistry of these combinations as it affects germicidal and insecticidal values, no safe *a priori* conclusions can be drawn. Even a laboratory test to determine these values must be carried out under rigidly prescribed conditions. Variations in the method may easily make the greatest differences in the results obtained.

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[AGRICULTURAL EXPERIMENT STATION OF THE RHODE ISLAND STATE COLLEGE, KINGSTON, R. I.]

THE AVAILABILITY OF THE INSOLUBLE NITROGEN IN CERTAIN COMMERCIAL FERTILIZERS.¹

By BURT L. HARTWELL AND F. R. PEMBER.

Received June 19, 1911.

Much uncertainty exists in the minds of agriculturists concerning the availability of the insoluble nitrogen in commercial fertilizers, because of the difficulty of recognizing the existence of material of low availability, such as leather, garbage tankage,

¹ Paper read at the Indianapolis meeting of the American Chemical Society.

¹ "Disinfection and Disinfectants."

and peat, after they have been subjected to certain processes of manufacture.

Since the effect upon plants must be relied upon as furnishing authoritative information regarding the value of manurial substances, it was decided to secure by pot experimentation some knowledge concerning the actual value of the water-insoluble nitrogenous ingredients of certain commercial fertilizers.

Of the brands collected during the regular inspection of 1908, certain ones which had a fairly high percentage of nitrogen in organic matter, and which represented different manufacturers, were selected. Most of them were potato and vegetable fertilizers, and were the higher-priced brands.

They were thoroughly leached with warm water, by decantation and on the filter, to extract especially the nitrates and ammonium salts, but the soluble organic nitrogen was of course also extracted. The residues were dried, the nitrogen determined,¹ and the material used in comparison with dried blood (13.62 per cent. N) and nitrate of soda, on an equal nitrogen basis, as sources of nitrogen for oats, millet, and oats grown successively on the same soil.

Optimum amounts of lime, potassium and phosphorus were provided for each crop in order that the differences in growth might be attributable to differences in the availability of the nitrogen.

Eight-inch Wagner pots and a light soil which it was hoped was naturally deficient in nitrogen, were used. The soil was found to be less deficient than was estimated, however, so that the first crop of oats was too well supplied with nitrogen to enable marked differences in availability to be shown. For the succeeding crops less nitrogen was used, so that less than the optimum amount should be present in those pots which had the uniform application.

The crop results are given in the accompanying table.

The addition of an extra amount of lime to two of the pots of soil which received blood increased the total yield of the three crops only from 302 to 305.9 grams. It is evident, therefore, that the general application of lime was sufficient. On the other hand, when the regular application of nitrogen in the blood itself was increased, the total yield rose to 348.2 grams, indicating that the general nitrogenous manuring was not sufficient for the production of maximum crops. If such had not been the case there would be no proof that an opportunity had been afforded for the materials under comparison to have exerted their full effect.

Although the leaching would remove all of the soluble phosphorus and potassium there would still remain much phosphorus in the reverted and insoluble condition which would exert an effect upon the crop unless this element was so abundantly supplied as to render impossible any additional influence from this source. In consideration of this, a very liberal application of acid phosphate was made for each crop, and yet when 50 per cent. more was added in connection with the general application of nitrogen

in nitrate of soda (see the last two series in the table), the total yield was somewhat increased, namely, from 338.9 to 357.5 grams. It is believed, however, on account of the fact that the other nitrogenous materials were less available than the nitrate of soda, that the full requirement for phosphorus was probably fulfilled by that which was added in the general application of acid phosphate; and that, practically what was present in the nitrogenous materials was without effect, especially on the last crop.

Results from an equal amount of nitrogen in nitrate of soda, dried blood, and the water-insoluble nitrogen of certain commercial fertilizers (Nos. 1-12):

Source of nitrogen.	Grams of air-dry crops.				Availability of nitrogen.	
	Oats, total.	Millet, total.	Oats		By last out crop, with blood at 80.	By alk. KMnO ₄ method
			Total.	Grain.		
None.....	{ 38.5 48.0	{ 16.7 14.7	{ 25.5 23.5	{ 8.0 8.2	0	
1.....	{ 64.5 69.0	{ 23.6 21.6	{ 43.5 45.5	{ 14.6 15.7	58	70
2.....	{ 69.5 83.0	{ 24.3 21.2	{ 42.0 45.0	{ 14.2 14.0	55	59
3.....	{ 73.5 71.0	{ 24.2 21.5	{ 50.0 51.5	{ 16.8 17.5	76	74
4.....	{ 78.5 75.0	{ 21.3 23.0	{ 51.0 51.0	{ 17.5 17.9	77	74
5.....	{ 71.0 78.5	{ 24.0 21.5	{ 52.5 55.0	{ 18.2 19.6	85	78
6.....	{ 74.5 74.5	{ 27.3 27.7	{ 49.5 49.0	{ 17.3 17.1	72	76
7.....	{ 78.0 68.0	{ 25.7 23.0	{ 53.0 56.0	{ 18.1 18.2	87	76
8.....	{ 78.5 85.5	{ 26.0 22.5	{ 45.0 47.0	{ 15.0 15.9	63	73
9.....	{ 80.5 82.5	{ 21.0 22.0	{ 49.0 51.0	{ 14.3 16.3	74	76
10.....	{ 76.0 77.5	{ 26.8 22.7	{ 54.5 53.0	{ 17.0 18.6	85	83
11.....	{ 82.5 77.5	{ 22.9 24.7	{ 52.5 51.0	{ 18.1 17.8	79	83
12.....	{ 85.0 86.5	{ 25.5 25.8	{ 53.0 51.5	{ 18.9 17.9	81	81
Dried blood.....	{ 78.0 67.0	{ 27.5 25.8	{ 52.0 52.0	{ 16.7 17.6	80	79
Dried blood + extra lime.....	{ 77.5 71.0	{ 30.0 25.7	{ 56.2 45.5	{ 20.6 14.7		
Dried blood (extra amount).....	{ 91.5 80.0	{ 28.4 31.3	{ 58.0 59.0	{ 20.8 21.8		
Nitrate of soda.....	{ 86.5 75.0	{ 25.9 27.5	{ 64.0 60.0	{ 24.7 22.6		
Nitrate of soda + extra phosphate..	{ 87.5 85.0	{ 28.5 29.0	{ 63.0 64.5	{ 23.2 24.5		

The increase over the check pots, caused by the general application of nitrogen in the dried blood, has been placed arbitrarily at 80 in the table, because of our belief that high-grade blood under conditions favorable to nitrification will cause an average increase in crop of about 80, in comparison with nitrate of soda at 100.

It may be seen by comparing the weights of the crops grown on the different fertilizer residues, with those from an equal amount of nitrogen in dried blood, that with a few exceptions the availability of the nitrogen in them was practically equal to that in blood.

This fact should increase the confidence of the

¹ The authors are indebted to Mr. J. Frank Morgan for this work.

agriculturist in the quality of the material in the more concentrated commercial fertilizers such as those used in this experiment.

In the following respects the best comparison of the different materials is afforded by the growth of the last crop, namely: the soil itself had become more depleted of its nitrogen; the cumulative effects of three applications of nitrogen were exerted; there was scarcely any evidence that the phosphorus associated with the nitrogenous materials exerted any influence; and the grain was allowed to ripen.

On the basis of the last crop, only five of the twelve fertilizers (Nos. 1, 2, 6, 8 and 9) yielded in each of the two respective pots, less total crop and grain than was produced in either of the pots in which blood was applied. Although the insoluble nitrogen in fertilizers 1 and 2, particularly, was less available than the nitrogen in blood, there is reason for the belief that it was largely from bone and meat tankage instead of from such low-grade material as garbage tankage, peat, and leather.

The directors of certain northeastern stations announced in March, 1910, their intention to have the fertilizers collected in 1911 for inspection, examined by some uniform laboratory method as to the availability of their organic nitrogen; and they appointed a committee of station chemists to recommend a method.

It was very opportune that the vegetation results under discussion had already been secured on the insoluble organic nitrogen of certain fertilizers, and that some of the identical material was on hand. This material was submitted, without any information concerning the crop results, to Mr. C. H. Jones, of the Vermont Agricultural Experiment Station, for the determination of availability by the alkaline permanganate method. The agreement was very satisfactory, but it was considered unfortunate that probably none of these particular fertilizers were made up of low-grade materials. Subsequently, however, a few decidedly low-grade fertilizers were likewise compared, with gratifying results; the vegetation tests are not fully completed and will not be published at this time.

The alkaline permanganate method was the one adopted March 4, 1911, by the agricultural experiment stations of New York, New Jersey and the New England States for "examining the activity of the organic forms of nitrogen," and a circular was printed which includes the details of the method.

In the last column of the accompanying table we have included the results secured by Mr. Jones with the method as adopted. The agreement is quite good even without full recognition of the fact that the limit of error in vegetation experiments must be placed rather wide.

Even the third crop (oats) equaled 49 grams on the check pots, although the pots to which blood was added yielded 55 grams more; this is taken to represent a range in availability from 0 to 80; it is evident, therefore, that even a variation of 3.4 grams in the weight of the crop from two parallel pots represents a difference of 5 in availability.

With two kinds of crops even on the same soil, the degree of availability will vary considerably, and on different soils the variation may be expected to be still greater. It is probable, for example, that an experiment with rye on an acid soil, in which the predominating microflora is composed of fungi and yeasts, would result in quite a different availability from one with barley on a neutral or alkaline soil in which bacterial growth is the more prominent. Two nitrogenous materials might exhibit very different relative availability, depending upon which of the above-mentioned conditions existed.

An availability test even with a single kind of plant and soil may comprise the following: one manuring and one planting; one manuring, and more than one planting; or more than one manuring and as many plantings.

It should be understood, therefore, that a difference of at least ten per cent. in the availability as determined by pot experiments is not of much significance, especially when no standard conditions have been adopted for carrying on vegetation tests.

The degree of availability of a substance, whether determined by vegetation or chemical tests, should be considered only as an approximation which is useful in distinguishing between materials of quite different qualities.

THE NATURE OF SOME COAL DUSTS AND MINE AIR FROM COLORADO MINES.

By JOHN B. EKELEY.

Received May 2, 1911.

In November, 1910, Governor John F. Shafroth appointed a commission, consisting of Victor C. Alderson, president of the State School of Mines; James Dalrymple, state coal mine inspector; R. D. George, state geologist and professor of geology at the University of Colorado; and John B. Ekeley, professor of chemistry at the University of Colorado, to inquire into the condition of the coal mines of Colorado, and the causes of the many accidents in those mines, and to suggest remedial legislation for the consideration of the Eighteenth General Assembly of the State.

The following tables give the analyses of samples of coal dusts and of mine air taken during the investigation trip made by the Coal Mine Commission.

The coal dust samples were passed through 20-, 100-, and 200-mesh sieves, and the fractions analyzed. In the fractions passing through the 200-mesh sieve, the analyses show a slight error, because the very fine dust undoubtedly lost some moisture during the screening operation. However, the results for this fine dust are very interesting, because they show that in all cases the composition was approximately the same as in the coarser portions. The analyses show that the non-carbonaceous part of the dust was of about the same state of division as the coal dust itself.

The air samples were collected by allowing water to run out from completely filled glass bulbs, which were then closed air-tight. This is the method used by Mr. Chamberlin, of the United States Geological Survey. The small amount of water remaining on

the inner walls of the bulbs absorbs carbon dioxide so that the amounts of carbon dioxide shown in the analyses are a fraction of a per cent. too low. The striking fact shown by the analyses is the presence, in most cases, of a small amount of methane, even in samples where none was expected. Since it is known that a small amount of methane may act as a primer in an explosion of coal dust, these facts are significant.

ANALYSES OF COAL DUST.

No.	Standard mine.	Mesh.	Mois- ture.	Volatile matter.	Fixed carbon.	Ash.
1	Main north entry, 250 ft. from hoisting shaft. Road dust.	{ 20 100 200	{ 13.2 11.5 8.0	{ 25.8 24.4 23.9	{ 33.3 30.1 28.5	{ 27.7 34.0 40.6
2	Same as No. 1. Dust from timbers.	{ 20 100 200	{ 9.7 8.5 8.0	{ 21.8 20.8 21.3	{ 25.1 27.2 26.0	{ 43.4 43.5 44.7
3	Fifth northwest room 8, 25 ft. from working face.	{ 20 100 200	{ 15.8 12.4 10.1	{ 24.6 22.2 22.3	{ 27.2 21.9 26.8	{ 22.4 34.5 40.8
4	Fifth southwest.	{ 20 100 200	{ 16.9 14.8 14.3	{ 26.1 26.7 27.0	{ 44.3 43.5 42.4	{ 12.7 15.0 16.3
5	Intersection of main south and first southwest entries. Road dust.	{ 20 100 200	{ 13.8 10.5 9.1	{ 24.0 25.3 25.1	{ 35.9 31.2 29.5	{ 26.3 33.0 36.3
6	No. 7, parting main south. Road dust.	{ 20 100 200	{ 16.8 13.7 12.7	{ 23.8 22.1 24.5	{ 37.5 22.0 28.0	{ 21.9 31.2 34.8
7	Main south at intersection of third east. Dust from timbers and ribs.	{ 20 100 200	{ 11.9 11.1 8.9	{ 22.1 20.2 22.8	{ 20.1 21.5 29.1	{ 35.9 37.1 39.2

Hastings mine.

8	Dust from main slope 600 ft. in. from timbers and ribs.	{ 20 100 200	{ 1.8 1.5 1.3	{ 28.9 28.6 25.7	{ 48.7 49.2 51.5	{ 20.6 20.7 21.5
9	Main slope between second and third entries. Road dust.	{ 20 100 200	{ 2.4 1.7 1.4	{ 27.8 28.3 26.3	{ 46.2 46.4 48.4	{ 23.6 23.6 23.9
10	Rope parting in main slope between 4th and 6th south. Road dust.	{ 20 100 200	{ 2.1 1.6 1.3	{ 23.8 24.4 23.6	{ 34.9 36.8 39.9	{ 39.2 36.2 35.2
11	7th south, 500 ft. from main slope. Trolley.	{ 20 100 200	{ 1.8 1.8 1.4	{ 17.9 18.9 19.0	{ 30.6 31.8 33.2	{ 49.7 47.5 46.4
12	Double parting between 7th and 8th cross-cut of 7th south. Road dust. Trolley.	{ 20 100 200	{ 1.9 1.8 1.6	{ 9.6 12.8 13.0	{ 16.0 19.9 22.2	{ 72.5 65.5 63.2
13	Dust from timbers and ribs between 1st and 2nd cross-cut in 7th south.	{ 20 100 200	{ 2.2 1.8 0.8	{ 21.7 21.1 22.0	{ 32.8 33.9 34.4	{ 43.3 43.2 42.8

Delagua mine.

14	Fine dust from ribs 3rd north entry, not dislodged by explosion.	{ 20 100 200	{ 2.4 2.3 1.1	{ 21.0 20.0 22.1	{ 39.9 40.3 39.2	{ 36.7 37.4 37.6
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Primero mines.

15	1st east mine. Dust from ribs, 700 ft. from entrance.	{ 20 100 200	{ 1.0 1.0 0.5	{ 24.4 24.8 25.3	{ 47.9 46.4 47.2	{ 26.7 26.2 26.1
16	1st north mine. Dust from ribs in A-12.	{ 20 100 200	{ 2.4 1.7 0.6	{ 20.5 18.1 21.7	{ 48.0 54.6 42.1	{ 24.7 25.6 26.6

Pictou mine.

17	Main slope 500 ft. in. Roof and ribs.	{ 20 100 200	{ 3.3 3.8 1.8	{ 25.0 23.1 28.2	{ 33.2 36.3 33.2	{ 38.5 36.8 36.8
18	8th north off main entry. Ribs.	{ 20 100 200	{ 5.3 5.2 2.3	{ 25.4 22.9 27.9	{ 36.2 38.5 34.7	{ 33.1 33.4 35.1

Danville mine.

19	Main slope 600 ft. from entrance. Ribs.	{ 20 100 200	{ 9.0 8.6 5.6	{ 39.1 33.5 34.9	{ 33.0 38.5 30.2	{ 18.9 19.4 19.3
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ANALYSES OF COAL DUST (Continued)

No.	Summit mine.	Mesh.	Mois- ture.	Volatile matter.	Fixed carbon.	Ash.
20	Bug dust, 8th southwest.	{ 20 100 200	{ 18.0 16.8 16.8	{ 21.0 21.0 21.0	{ 54.1 54.3 54.3	{ 6.9 7.9 7.9
	Somerset mine					
21	Coarse, quite damp stuff from ribs.	{ 20 100 200	{ 7.8 6.4 6.4	{ 26.8 24.3 24.3	{ 49.3 49.4 49.4	{ 16.1 29.9 29.9
	Vulcan mine					
22	Main entry, 300 ft. in. Dust from ribs.	{ 20 100 200	{ 6.2 6.0 3.5	{ 25.9 27.9 33.0	{ 49.1 47.0 43.7	{ 19.8 19.1 20.8
23	Main entry, opposite 8th B, up-raise. Ribs.	{ 20 100 200	{ 11.5 6.4 1.6	{ 25.8 33.6 32.9	{ 54.2 49.5 43.6	{ 9.5 11.5 12.9
	Rockvale mine.					
24	Dust from ribs of 5th south.	{ 20 100 200	{ 15.4 12.2 3.1	{ 10.2 12.8 17.9	{ 20.9 19.6 11.6	{ 53.5 56.4 57.4
25	Dust from road in 5th south. Same place as No. 24.	{ 20 100 200	{ 9.8 9.2 5.0	{ 13.4 13.8 17.3	{ 19.1 21.7 19.0	{ 49.7 55.3 58.7
26	Dust from timbers, main south entry, 1,500 ft. from shaft.	{ 20 100 200	{ 7.2 5.7 2.9	{ 19.7 21.2 26.1	{ 39.6 39.0 34.9	{ 33.5 34.1 36.1

ANALYSES OF MINE-AIR SAMPLES.

	Standard mine.	CO ₂ .	O.	N.	CH ₄ .
1	Fifth northeast, Main intake ¹ north side.....	0.25	17.4	82.35
2	Fifth northwest, room 8.....	20.8	79.2
3	Fifth southwest, 30 min. after shot.....	0.61	19.7	79.69
4	Ninth southwest, 100 ft. from main entry.....	20.5	79.04	0.46
5	Main south, 7th double parting.....	20.0	80.0
	Hastings mine.				
6	Main slope, 300 ft. from mouth.....	19.7	80.3
7	7th south double parting.....	20.4	78.5	1.1
8	1st dip off 7th south, shot night before.....	20.4	79.6
9	7th south at 7th crossing.....	20.4	79.6
10	Face of 7th south, pillar work.....	20.4	79.6
	Primero 1st east mine.				
11	Room 8, B-9, west.....	20.6	79.4
12	Intersection B-9 east and main-air course.....	0.4	20.6	79.0
13	Main return 1,000 ft. from fan ..	0.7	19.9	79.4
	Primero 1st north mine.				
14	Room 3, first blind A-12.....	20.6	79.2	0.2
15	Room 6, A-11.....	0.1	20.5	79.4
16	Main air course, 75 ft. outside A-7, overcast.....	20.2	79.8
	Cokedale mine.				
17	Room 10, 2nd B west, pillars.....	20.0	79.3	0.7
18	Face of 5th west C.....	19.8	79.4	0.8
19	Main return under 4th south undercast.....	20.0	79.6	0.4
	Pictou mine.				
20	Face of room 5, 4th cross off 8th south.....	19.7	80.3
21	Bottom of slope, face.....	20.5	78.4	1.1
22	Face of 10th north.....	19.7	79.9	0.4
23	Back entry, intermediate air course, 7th south.....	19.4	78.8	1.8
	Danville mine.				
24	Face of main slope.....	18.5	81.1	0.4
25	Main slope just above 7th south, above fire.....	0.3	20.5	79.2
	Summit mine.				
26	Main return, 100 ft. from shaft.....	19.9	80.1
27	Room 11 off 7th southwest.....	0.2	20.1	78.9	0.8
28	Face of 7th southwest.....	20.0	79.7	0.2
	Somerset mine.				
29	Room 40, 6th west.....	20.5	78.1	1.4
30	Room 2, 9th west.....	20.2	78.8	1.0
31	Main entry, 9th west.....	0.1	20.4	79.5
32	Face of main slope.....	20.1	78.7	1.2
33	Main return, 75 ft. from fan.....	0.2	20.6	78.8	0.4

ANALYSES OF MINE-AIR SAMPLES (Continued).

	Vulcan mine.	CO ₂ .	O.	N.	CH ₄ .
34	Face of workings, main entry, 600 ft. in.....	20.5	78.9	0.6
35	No. 9-B upraise, 25 ft. from entry	0.6	20.1	78.7	0.6
36	Cross-cut between 8-B and 9-B upraises.....	0.4	20.5	78.5	0.6
	Rockvale mine.				
37	Room 28, C dip.....	0.2	20.0	78.6	1.2
38	1st dip, 5th south, off C dip.....	19.8	78.9	1.3
39	Main return in main south, 1,500 ft. from shaft.....	19.7	79.1	1.2

The dust samples from the Standard and the Summit mines, which are probably representative samples of dusts from the Boulder County field, show a fairly high percentage of moisture. This would tend to make these dusts safer than those of the southern fields, which are very dry. However, it would be dangerous to trust to this for safety from explosions, since we have not enough data on this question as yet. These dusts from the ribs and timbers and from the roadways usually contain considerable fire clay, but the results from experiments at the Pittsburg testing station on similar coal dusts containing a high percentage of fire clay have shown that even such dusts are dangerous.

The dusts in the mines in the southern part of the state are without doubt very dangerous. A similar dust having a composition, moisture 3.41, volatile matter 17.98, fixed carbon 47.22, ash 21.39, was tried in the explosion gallery of the Pittsburg testing station. The dust exploded from the effect of a blown-out shot of 500 grams of black powder, and propagated the flame through the entire length of the dusted gallery, and 27 feet beyond the dust zone.

Similarly, a road dust, rich in rock dust, giving the following analysis, moisture 2.75, volatile matter 15.45, fixed carbon 24.85, ash 56.95, exploded and propagated the explosion 20 feet beyond the dust zone. All the dusts in the tables except Nos. 12, 24 and 25 would be far more likely to explode than the samples experimented upon at Pittsburg, as may be seen by comparing the analyses.

An interesting dust is No 14, which was taken from a sheltered place on the ribs of the third north entry of the Delagua mine, and which had not been dislodged by the explosion. This may be taken as a fair sample of the Delagua mine dust, which, without doubt, contributed its share to the explosion of October 8th. This dust varies little in composition from the dust found in the other mines of that part of the state.

It is a pleasure to say that, in the Cokedale mine, there was very little dust; in fact, no suitable sample for analysis was found. In the Somerset mine there was practically no dust, though, after some trouble, a sample was obtained.

Of the mines visited, almost all were in danger from coal dust, and it is fair to assume that the great majority of the mines of the state are in the same condition. This matter should be remedied by proper legislation, requiring that the dust be rendered harmless by means of the addition of a large amount of

¹ The intake is contaminated by air from some old workings.

moisture, and possibly by the removal of the resulting mud from the mine.

UNIVERSITY OF COLORADO.

[CONTRIBUTION FROM DIVISION OF DRUGS, BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE]

THE QUANTITATIVE DETERMINATION OF KETONES IN ESSENTIAL OILS.

By E. K. NELSON.

Received June 7, 1911.

While we have general methods for the estimation of alcohols, esters, phenols and aldehydes in oils, such a method seems to be wanting in the case of ketones. Some substances of this class, as for example, camphor, do not react with sodium bisulphite. Other while they may react with bisulphite, can not be even approximately estimated by its use.

The methods of Sadtler¹ and Labbé,² while valuable in many cases, could not be accepted as general methods because the reactions involved are not characteristic of all ketones.

All the ketones usually found in essential oils, however, do react with hydroxylamine to form oximes. The method of Walther³ depending upon the transformation of the ketone into oxim on boiling with standard alcoholic solution of hydroxylamine hydrochloride in the presence of alkali, and the determination of the amount of the reagent thus consumed by titration of the excess on completion of the reaction seemed to offer advantages as a general method for the analysis of ketone-bearing oils. Walther experimented on the estimation of citral and carvone, but does not speak of having tried the method on other ketones, or aldehydes. The following work was undertaken to test the accuracy of Walther's method for ketones in general. The ketones used were prepared from the oils in which they occur, or were obtained in some cases on the market and purified. In every case the method was carried out the same way. The standard hydroxylamine solution was prepared by dissolving 20 grams hydroxylamine hydrochloride in 30 cc. water and adding 125 cc. aldehyde-free alcohol. One to two grams of the substance were boiled in a water bath under a reflux with 35 cc. of the reagent and 2 grams sodium bicarbonate, cooled, 5 cc. HCl added, through the condenser, followed by water and the mixture made up to 500 cc. The solution was filtered and in an aliquot part of the filtrate the free acid was neutralized by running in $N/2$ NaOH, using methyl orange. Phenolphthalein was then added and the hydroxylamine left in excess of that required to form oxim was titrated with $N/10$ NaOH. The results in the following table were obtained:

Considering the nature of the work and the difficulty of preparing absolutely pure materials to start with, these results may be considered as fairly satisfactory except in the case of fenchone. As this is a rather rare ketone, however, and as it is present in but few oils and in those only in small amount, a method for its estimation is not so necessary.

¹ *Am. J. Pharm.*, 76-84; *J. Soc. Chem. Ind.*, 23, 303.

² *Bull. Soc. Chim.*, 23, 283.

³ *Pharm. Centr.*, 41-613.

Ketone or (aldehyde)	Wt. substance.	35 cc. reagent require $N_{10}NaOH$.	Excess reagent require $N_{10}NaOH$.	Time of boiling, Hrs.	Amount of substance returned per cent.
Carvone.....	2.3508	605.5	455.5	1/2	96.18
Carvone.....	2.3343	605.5	454.5	1	97.51
Carvone.....	2.2819	605.5	455.0	1	99.41
Carvone.....	1.9493	607.8	479.5	1/2	99.12
Pulegone.....	2.2852	605.5	452.5	1/2	101.77
Pulegone.....	2.3228	605.5	451.5	1	100.77
Camphor.....	1.025	1	92.3
Camphor.....	1.0626	1	97.13
Camphor.....	2.0509	2	99.08
Camphor.....	1.7177	2	101.5
Thujone.....	2.2793	604.6	459.0	1/2	97.1
Thujone.....	2.2903	604.6	458.0	1	97.3
Menthone.....	2.1416	1	97.5
Fenchone.....	0.9026	578.2	527.3	2	85.7
Fenchone.....	1.1823	578.2	540.6	1	50.6
Benzaldehyde.....	2.5447	606.7	375.0	1/2	96.5
Benzaldehyde.....	2.5278	606.7	376.0	1	96.7

In the case of spearmint oil the Walther method was tried in comparison with the estimation of the carvone by absorption in boiling sodium bisulphite solution as well as by the Labbé method.

RESULTS ON CARVONE; SPEARMINT OIL.

Sample.	Labbé method.	Walther method.	Absorption by boiling $NaHSO_3$.
1	54.7	58.4 53.1	55.0
2	61.3	65.5 66.4	67.5
3	61.43 60.7	61.5

A sample of tansy oil, assayed by the Walther method, gave thujone = 68.56 and 65.42 per cent. A sample of wormwood oil gave thujone = 33.15 per cent. and 31.24 per cent. Pennyroyal oil gave 81.87 per cent. ketone by this method calculated as $C_{10}H_{16}O$. A mixture of pulegone with at least two other ketones is present in pennyroyal oil. A sample of rosemary oil gave 30.33 and 30.24 per cent. ketone calculated as camphor.

The Walther method can not be recommended for the assay of any particular ketone-bearing oil until the influence on the reagent of other substances in the oil has been determined by working on known mixtures, and comparison, when that is possible, with other methods.

This work will require time. For the present it seems that the assay of oils in which carvone, camphor, pulegone or thujone is the main constituent can be carried out with fair accuracy by this method, at least affording a criterion of the purity of such oils.

THE MANUFACTURE OF AMMONIA IN BY-PRODUCT COKE OVENS.

By LOUIS CLEVELAND JONES

Received March 9, 1911.

Nitrogen is to me the most intensely interesting element of all the eighty with which we chemists have to deal. It is present in only small quantities within the solid earth's crust but in tremendous quantities in the atmosphere, enough if condensed upon the

earth's surface to submerge us all in a liquid layer only a little lighter than water and twenty feet deep. A sea of liquid nitrogen over all the surface of the earth gives you an idea of the abundance of this substance.

Uncombined, nitrogen is the most inactive and harmless material that can be imagined. It can be mixed in all proportions with oxygen and hydrogen and yet retain its passive characteristics.

Combined, however, chemically with 2.5 parts of oxygen (another harmless even life-sustaining element) it forms fuming nitric acid which would consume the human body with almost explosive violence. Combined with three parts hydrogen it forms ammonia gas, a volatile alkali almost as dangerous a substance as its oxygenated cousin. In other compounds it forms the most sensitive explosives, set off by the gentlest breath of air, or if we wish, explosives the most powerful and at the same time the most useful.

Man cannot live without nitrogen in his food, yet combined in a particular manner with carbon (another harmless substance) it becomes one of the deadliest poisons known. Combined, however, with carbon in another way but in the same proportion it is physiologically harmless. In yet another way nitrogen combined with hydrogen, oxygen and carbon produces all that wonderful galaxy of colors of which aniline and nitro compounds are the base.

Uncombined, it requires the subtlest means (nitrifying bacteria) or else the most strenuous (the electric arc) to bring it into chemical union, but when once combined with other elements it forms the most stable of chemical compounds.

To illustrate the sources and uses of the particular nitrogen compound, ammonia, which we are discussing to-night, I have prepared two tables.

Table I shows some general sources of ammonia; II indicates some of the principal forms in which it is obtained and their general uses.

TABLE I.—SOURCES OF AMMONIA.

By product coking of coal
By-product of producer gas manufacture
From distillation of peat.
From distillation of shale
Blast-furnace gases
Distillation of bones and leather.
Synthetically produced from $N_2 + H_2$ and osmium
From nitrides of metals, titanium nitride
From calcium cyanamide and steam
Found in alkali lakes and waters from volcanic rocks
Electric sparking of $N_2 + H_2$
Sewage and urine

In these two tables there is material for many days' discussion, but I propose to speak only of the production of ammonia in by-product ovens.

Production of Ammonia in By-Product Coking of Coal.—The yield of ammonia as sulphate in the actual coking operation varies from 18–28 lbs. per ton of dry coal. These look like rather small figures (about 5 lbs. NH_3) to be obtained from 2000 lbs. of coal, but the total annual production from by-product coke ovens in the United States alone amounts to the immense total as sulphate of ammonia, to about 75,000 tons; or at 25 tons to a car, 3,000 carloads, and at 50 cars each would equal 160 train loads, or a solid trainload 22 miles long. The total production

TABLE II.—AMMONIA BY-PRODUCT FROM COKING OF COAL.

	Sources.	Uses.
Weak liquor	From gas washers	Further manufacture
Crude liquor	From weak liquor	Manufacture of soda ash, felts, preserving timber
Partially refined liquor	From crude liquor	For explosives, ammonium nitrate
Liquor (partially purified liquid, free from sulphur)	From crude liquor	Synthetic cyanides, Ostwald process
Aqua	From crude liquor	Household and further mfg., refrigeration
Anhydrous	From crude liquor	Refrigeration
Ammonium sulphate	From crude (direct)	Fertilizers, further mfg.
Ammonium nitrate	From crude	For safety explosives
Ammonium chloride	From aqua (in S. A. process)	Electric batteries
Ammonium bicarbonate	From aqua and CO ₂ gas	Baking and baking powders, smelling salts, dyeing
Ammonium picrate	From aqua and picric acid	Explosives
Ammonium chlorate		Explosives
Ammonium sulphide	From aqua	For chemical analysis and photographic work
Oxalate and other salts		
Ammonium phosphates		
Ammonium chromates		
CaCl ₂ .8NH ₃		
"Dry ammonia"	(NH ₄) ₂ SO ₄ -Na ₂ CO ₃ , etc.	Cleaning and laundry
Ammonium oleate	Aqua and red oil	Ammonia soap
NH ₄ CN		Ore extraction (Au, Cu, Ag)

of the world is probably more than 1,000,000 tons as sulphate. Thus does this little 5 lbs. of NH₃ ($\frac{1}{4}$ of 1 per cent. of the coal coked) make a great aggregate.

Nitrogen, of course, in the coal is the source of the ammonia produced from coal.

We have tested the nitrogen content in average samples of coal representing all the coal used during a month at several of the Semet-Solvay plants.

TABLE III.—NITROGEN IN COALS COKED DURING JUNE, 1907.

Plant.	(Tests by Cole.)			% Nitrogen in coke.	
	% Nitrogen in coal.				
A	1.104	1.214	1.104		
B	1.21	1.20			
C	1.29	1.32		1.104	1.11
D	1.38	1.39		1.518	1.49
E Boomer	1.24	1.16			
Smokeless	1.46	1.34			
F	1.21	1.22			
G	1.36	1.36			
H	1.33	1.35			
I	1.17	1.21		1.186	1.104
J	1.38	1.33		1.104	1.131
K	1.076	1.269	1.242	0.966	0.993
Coalite	1.20			1.29	1.331

Distribution of Nitrogen in the Coking Process.—It will be observed that the nitrogen in the coke produced at Plant D (on the basis of 76.7 per cent. coke yield) exceeds that in the coal—obviously an error, probably due to a non-representative or contaminated coke sample. As a general rule we have found that the nitrogen in the coke runs about 90 per cent. of that found in the coal.

From the above table the nitrogen in a ton of coal was distributed as follows:

TABLE IV.—NITROGEN BALANCE FOR OPERATION AT S. S. CO. PLANT C.

	Calculated to (NH ₄) ₂ SO ₄ .
	lbs.
Coal, 1.30 per cent. $\times 4.7$ ($\times 2000$).....	122.6
Ammonia yield, actual.....	25
Nitrogen in coke.....	78.2
Gas 10,500 cu. ft. = 300 M ³ containing 5 per cent. N = 4.5 K.....	10.0
Tar 90 lbs. 0.8 per cent. N = 0.72 lbs. $\times 4.7$	3.5
Pyridine 0.3 Gpl in 0.5 M ³ = 0.15 K $\times 0.83 \times 22$	0.3
Simple cyanides.....	0.2
Methyl cyanides.....	0.2
	119.6
Loss.....	3.0

Using nitrogen in coke as 90 per cent. of that in coal.

TABLE V.—NITROGEN BALANCE FOR PLANT D.

	lbs.	lbs.
Coal, 1.385 per cent. $\times 4.7 = 6.5 \times 2000$		130.0
Actual ammonia yield.....	27	
Nitrogen in coke.....	90	
Nitrogen in gas.....	10	
Tar, pyridine and cyanides.....	5.9	132.9
Excess.....		2.9

Likewise making the nitrogen balance for the other plants we get the following figures:

TABLE VI.

Plant.	Total N in coal as sulphate. lbs.	Total N in products as sulphate.
A.....	114.0	113.2
B.....	113.2	114.3
E.....	121.2	124.4
F.....	114.3	115.1
G.....	127.8	127.0
H.....	126.0	126.2
I.....	111.8	112.4
J.....	127.5	126.2
K.....	118.0	116.7

Percentage Recovery.—It is evident thus that of the total nitrogen in coal only about 20–25 per cent. is recovered as ammonia in the by-product operation. If, however, we consider the nitrogen remaining in the coke to belong to the province of the blast-furnace man, we may state with greater satisfaction to the by-product operation that only 8–10 per cent. of the total nitrogen of a coal is lost in the by-product operation. Stating the same in another way, of the total volatile nitrogen the by-product operation recovers 62 per cent. as ammonia, 14 per cent. as cyanides and other nitrogen compounds, 24 per cent. being lost as nitrogen gas.

Loss in Gas.—Since the presence of each percentum of nitrogen produced in illuminating gas represents a loss of sulphate of ammonia equal to two pounds per ton of coal, it would be of importance (though no method has been suggested) to decrease the amount of nitrogen evolved with the gas.

Loss in Coke.—The greatest portion of the nitrogen in a coking coal, *i. e.*, 60–70 per cent., escapes with the coke where it exists in an unknown combination

until liberated by the burning of the coke in the cupola or blast furnace.

We have no information regarding the chemical compound which retains the nitrogen in coke so persistently, *i. e.*, when heated even to 1000–1100° C. Possibly it is there as an inorganic nitride formed with the ash of the coke or absorbed as cyanamides formed from some inorganic carbides derived from superheated carbon and ash. It is probable, however, that it may be held by the carbon alone since the coke made from oil residues or pitch, though free from ash, still contains nitrogen to the extent of about a per cent.

Nitrogen may be completely recovered from coke by heating with soda lime.¹

Combined Nitrogen in the Blast Furnace.—When the coke goes to the blast furnace containing about 1.1 per cent. nitrogen, there is formed from this nitrogen, under certain conditions in the reducing blast-furnace gas, considerable ammonia which in Scotland is recovered by washing the gas in acid.

Ammonium chloride stalactites from the chlorides in the ore have been found hanging from some of the pipes carrying waste blast-furnace flue gases.

Likewise cyanogen is formed in blast-furnace gas near the bottom of the furnaces as high as 15.5 grams per M³, equivalent to about 211 lbs. sulphate of ammonia per ton coke. About 71 lbs. are reported by Bell² in the exit blast-furnace gases. The first figure is far above theory for the total nitrogen. The evidence is therefore strong that there is at times at least an actual synthetic production of cyanogen from atmospheric nitrogen and carbon in the blast-furnace operation.

By-Product Operating Conditions.—In order to get high ammonia yields in the by-product coking operation we have to consider the following factors in the coal quality:

- (1) The amount of nitrogen in the coal.
- (2) The amount of volatile nitrogen, *i. e.*, the total nitrogen in the coal less that retained in the coke.
- (3) The amount of volatile matter.
- (4) The nature of the volatile matter.
 - (a) As to oxygen content (water and oxygenated gases evolved).
 - (b) As to calorific value.
- (5) The amount and nature of the coal ash itself—CaO, Fe₂O₃.

I will discuss briefly these factors in the quality of a coal which affect its yield of ammonia.

First, the Amount of Total Nitrogen.—This varies greatly in various coals as given by the tests of the U. S. Fuel Testing Bureau.

Some Texas and N. Dakota lignites and a Morgan Co. Mo. coal contain as low as 0.71–0.75 per cent. nitrogen. On the other hand, coals from Straig Creek, Eastern Ky., from the Rock Island Coal Co., Indian Territory and a smokeless coal from Rush Run, West Va., contain 1.70–1.85 per cent. nitrogen.

Natural asphalts contain 1.0–1.1 per cent. nitrogen. In by-product tar and pitch about 1 per cent. N has been found. In fact we have been able to obtain experimentally an ammonia yield as sulphate of 8–10 lbs. per ton from hard by-product pitch.

Second, Volatile Nitrogen.—No effort, as far as I know, has ever been made to determine the amount of volatile nitrogen in coals and its relation to ammonia yields. From this volatile nitrogen, of course, must come all the ammonia and other valuable nitrogen compounds. Unfortunately the nitrogen in the coke has rarely been determined, but the figures obtained by us show a definite relation between the amount of volatile nitrogen and ammonia yields. In practice the recovered ammonia with the other nitrogen compounds in the weak liquor plus the nitrogen in the gas would give the measure of the volatile nitrogen, but unfortunately the nitrogen in the gas commercially produced is seldom quite free from atmospheric nitrogen and flue gas nitrogen, due to leaks and the porosity of the coking chamber.

From experiments made in the bomb apparatus devised in our laboratory we have indications that the amount of uncombined nitrogen evolved in the gas is, for all the conditions of temperature commonly used in the production of illuminating or coke oven gas, practically a constant percentage. Samples of gas tested under conditions absolutely preventing contamination with flue gas or atmospheric nitrogen show the nitrogen content to be about constant all through the coking period, although it has been often stated that the gas evolved towards the end of the coking period consists largely of nitrogen.

Even under conditions of extremely low temperature, *i. e.*, producing coalite, considerable free nitrogen is evolved with the gas, while the unevolved nitrogen, *i. e.*, that in the coalite itself, is higher than in the original coal, since under these conditions a greater amount of nitrogen remains in the coke.

On account of the meager information at hand we are continuing the further investigation upon the volatile nitrogen in coal, and the conditions which increase its total as well as the proportion of the combined compared with the uncombined volatile nitrogen.

Third, Amount of Volatile Matter in a Coal.—In general the ammonia yield increases with the percentage of the volatile matter in the coal coked, though the nature of that volatile matter as regards volatile nitrogen, oxygen content and calorific value is influential.

Fourth, Nature of the Volatile Matter.—(a) In fact there are strong indications that the presence of oxygen in the volatile matter of a coal, though tending to produce poor coke structure, has a beneficial influence upon the yields of ammonia. It appears that the evolving moisture actually produced *in situ* at the carbonizing temperature either by dilution or other protecting influence tends toward a higher yield of ammonia.

(b) Early realizing the influence of oxygen in the volatile matter as determined by ultimate analysis, which as you know is a time-consuming and difficult

¹ "Ammonia and Its Compounds," Camille Vincent, *Trans.*, 1901, M. J. Salter, p. 44.

² Bell, "Principles of the Mfg. of Iron and Steel."

operation, and at best throws the combined errors upon the most influential constituent, oxygen, we have devised a simple method of calculation from the proximate analyses and calorific value to indicate the quality of the volatile matter in a coal; for, as you know, this is the factor that not only determines the character of the coke but also as well the amounts and quality of the by-products to be expected.

On the basis of this calculation we have been accustomed to classify coals according to the calorific value by per centum of volatile matter, as well as according to the total amount of volatile matter.

In the table following are arranged some typical coals in the order of their calorific value per unit of volatile matter. This order has also been found to be in accord in a measure with the behavior of these coals under the influence of heat.

TABLE VII.—CALORIFIC VALUE BY PER CENT. VOLATILE FOR SEVERAL TYPICAL COALS.

Coals.	H ₂ O.		Vola- tile.	F.	Ash.	Sul- phur.	Phos- phorus.	Cal. val.	
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Cal. val.	per cent. vol.
A.....	1.36	25.10	66.08	7.46	0.61	0.005	7907	105.5	
B.....	2.52	24.76	64.34	7.38	0.80	0.011	7787	105.0	
C.....	0.95	22.37	73.48	3.20	0.72	0.005	8242	103.9	
D.....	..	26.44	67.06	6.50	0.87	..	8107	103.7	
E.....	..	26.12	66.75	7.13	0.95	0.018	7960	102.9	
F.....	..	25.10	66.60	8.30	0.85	0.016	7888	100.6	
G.....	1.23	32.27	61.05	5.45	0.77	0.015	7901	92.4	
H.....	1.61	37.04	55.70	5.65	1.22	..	7856	91.5	
I.....	1.18	35.82	58.54	4.46	0.63	0.003	7972	90.8	
J.....	2.00	35.05	58.50	4.45	0.63	0.004	7817	88.5	
K.....	2.05	36.43	51.48	10.04	2.30	0.024	7291	87.0	
L.....	6.66	36.48	48.46	8.40	1.30	0.006	7036	86.6	
M.....	6.71	37.17	51.72	4.40	0.72	0.007	7158	80.0	

Fifth, Ash.—Ash in a coking coal is in most cases only a diluent, an inactive impurity. When, however, consisting largely of iron oxide or calcium carbonate, it has an influence on the ammonia yields. Iron oxide in large amounts at high temperatures has a catalytic action upon ammonia gas and decreases its yield. Lime, on the other hand when present in considerable amounts, increases the expulsion of nitrogen from the coke.

GENERAL.

Operating Conditions which Affect the Yields of Ammonia, Cyanides, etc.—Since coals are generally, if not always, selected for coke- or gas-producing properties, cheapness and accessibility, and since the nitrogen, of course, in these given coals is the only source of ammonia, we strive to provide operating conditions which tend to keep as high as possible the amount of nitrogen volatilized (that remaining in the coke being of negative value); also we strive to have as great a percentage as possible of the volatilized nitrogen in the combined condition (principally ammonia).

Of course in those processes where the coke or coal is entirely consumed, *i. e.*, producers, it is possible to obtain a much higher yield of ammonia because all the nitrogen corresponding to that which in the by-product operation remains in the coke becomes available. Thus in the production of producer gas by the Mond process it is not unusual to obtain 80

lbs. ammonium sulphate per ton of coal. The actual yield in producers, however, when based upon the total nitrogen volatilized is not greater than in by-product ovens and the higher yield therefore from producer is not, as generally supposed, due to the lower temperatures.

The conditions in the coke ovens themselves which are under our control are:

Temperature.

Pressure.

Gas travel, height and fulness of ovens.

Introduction of foreign materials:

(a) Gas, steam, washed gas.

(b) Solids: iron oxide, lime.

LENGTH OF COKING PERIOD.

Temperatures.—Temperature is the chief factor in the by-product operation. Coal subjected to gradually increasing temperature after drying about 100° C. suffers practically no change until about 400° C., when it begins to decompose and give off gas and tarry matters. At about 430° C.—the temperature used to produce coalite—carbonization takes place producing about 8 lbs. sulphate of ammonia, a coke still containing 4–5 per cent. volatile matter (largely hydrogen) and a high percentage of nitrogen, a rather high yield of exceedingly light tar, and from four to four thousand five hundred feet of exceedingly high quality gas. The point which is of particular interest in this connection is that this gas seems to contain, as evolved, practically as much free nitrogen as if coked at higher temperatures. The ammonia yield being small and the other nitrogen compounds certainly not above normal, there remains the necessity in the coke a large portion of the nitrogen ordinarily volatilized. To speak of the temperature of coking is very misleading for the temperature of the retort during operation is different at almost every different point and at every different point of time. At the outside of the coking mass near the wall the temperature is perhaps 1100° C. while within the center of the coking mass not above 100–200°. From the beginning of the coking period the isothermal lines converge upon the center of the coking mass until the coking is complete and the coke is withdrawn.

As a measure of average temperature conditions therefore I have, to a certain extent, abandoned the thermometer or pyrometer and adopted other means, *i. e.*, gas analysis. This will appear from the following gas analyses from similar coals, one gas produced at low, the other at high temperatures.

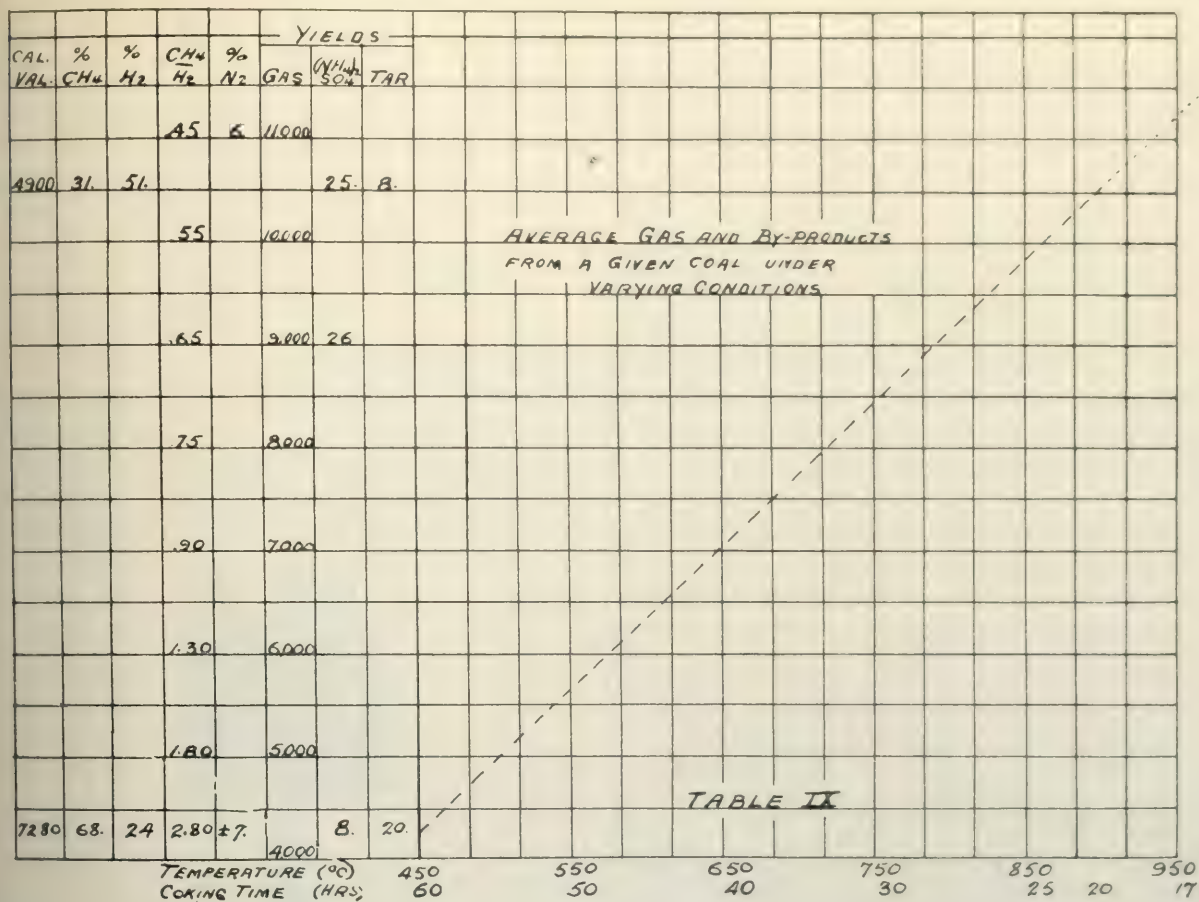
TABLE VIII.

	P. G. coalite gas.	Ordinary coke oven gas.
Temperature.....	430° C.	1050° C.
Coking period.....	60 hrs.	17.7 hrs.
Volume of gas.....	4260 cu. ft.	10500 cu. ft.
CO ₂	2.0%	1.7%
Illuminants.....	2.2	2.9
O ₂	2.3	0.6
CO.....	3.0	4.8
H ₂	21.2	51.6
CH ₄	60.1	31.3
N ₂	9.2	7.1
Calories per M ³	6397	4906
CH ₄ to H ₂	2.81	0.607
Combined O ₂	3.50	3.25

With this gas data outlined on Table IX we have an interpretation of each by-product factor in terms of the other; the conditions represented are merely suggestive, and as it chiefly concerns gas manufacture details are reserved for a general discussion of the manufacture of illuminating gas in by-product ovens.

a greater gas volume, generally of more value than the corresponding amount of tar destroyed.

Foreign Materials Effect upon Ammonia Yield.—In England the introduction of steam into the hot oven retort has been reported to give an increased ammonia yield. Further experiments in this direction



It is of interest, however, in the consideration of the nitrogen balance of the by-product operation, since it seems to indicate that low temperatures as well as high produce free nitrogen and that there is an average condition of temperatures which produces maximum ammonia yields.

Pressure.—Pressure in a by-product coking retort is of particular importance for regulation of leakage of gas outward or of flue gas inward through the porous walls of the oven.

The variation of the few millimeters from the 760 one way or the other necessary to regulate leakage is practically without effect upon any composition or decomposition of the by-products sufficient to influence yields.

Gas Travel, Height and Fulness of Ovens.—The gas and all other by-products, including ammonia, travel from the coking coal to the hot walls and along them to the gas outlet. The hot oven walls and coke have therefore opportunity for catalytic action tending to decompose both ammonia and the hydrocarbons of the gas. This action is not all bad, for a portion of the tar oils is at the same time cracked to produce

have not been encouraging. Of course the presence of steam may, acting as a diluent, protect the ammonia from the oven walls, but I suspect the greater amount of the small increase of ammonia arises from the nitrogen in the coke, due to actual consumption of the coke by the steam to form water gas.

The introduction of ammonia-free gas through the retort during the coking process doubtless protects both the gases and the ammonia but has never been found commercially practicable.

Iron Oxide.—Fine iron oxide in the form of flue dust, a waste product from blast furnaces, has been introduced into coke to enable its recovery with the consumed coke. Our tests indicate that the catalytic effect of iron oxide in a coke oven is sufficient to decrease the ammonia recovery to such an extent that the saving in flue dust in this way would result in actual loss.

Basic Oxides.—As already suggested, the presence of lime in a coking coal has been shown in English gas practice to increase the ammonia yield, but the fluxing action of lime upon the oven walls has made the practice of doubtful value. At any rate the English

retort gas makers who originally advocated the practice have abandoned it.

Whether the increased ammonia yield in this case is due to a greater expulsion of nascent nitrogen from the coke or to the prevention by the lime of the destructive catalytic effect of oxides of iron always present in the ash of coke has not been determined.

Length of Coking Period.—Whether the coke is pushed before the volatile matter is almost completely expelled or remains after the evolution of gas ceases is of more importance to the coke oven operator than to the coke consumer. The retention of coke in the ovens after complete evolution of gas is a waste in coke oven plant efficiency. If the last percentum of volatile matter, principally hydrogen, is not expelled, a comparatively large amount of gas, though of low

quality, is lost. On the other hand, if coke containing an additional amount of unexpelled volatile matter, principally hydrogen, goes to the blast furnace, little harm is done except that of a diluent since the hydrogen remains still uncombined in the blast-furnace exit gases where, of course, it is of value in case these gases are utilized for fuel or for gas engine power.

Recovery of Ammonia.—The ammonia present in the gas to the extent of about 100 grams NH_3 per M finally escaping from the conflicting influences of the hot retort is absorbed either in water to produce weak liquor, the source of all stronger ammonia liquors, or absorption of ammonia from the gas may take place in sulphuric acid direct to produce sulphate of ammonia.

LAB. OF SOLVAY PROCESS CO.,
SYRACUSE, N. Y.

PLANTS AND MACHINERY

AGITATOR FOR DETERMINATIONS OF SILVER, PHOSPHORUS AND MAGNESIA.

By L. W. BAHNEY.

Received June 1, 1911.

This machine (Fig. 1) was designed for rapid work in making assays of silver bullion by the Gay-Lussac method but it may be employed as a means of hastening precipitation in the determination of either phosphorus by the molybdate method or of magnesia as a phosphate.

The important feature is that of being able to place the bottles in, or remove them from, the clamps without stopping the machine, thus saving a lot of time and unnecessary trouble.

Nearly all of the apparatus in use as agitators are somewhat cumbersome in that the bottles or flasks, in which the determinations are made, are either placed in a box that has a cover that must be clamped down each time or they are placed in some sort of a clamp that must be tightened and loosened each time, and always when the machine is at rest.

The clamps are made of spring brass mounted on a brass disk that is operated by an eccentric having a speed of 450 revolutions per minute, and a small electric or water motor is sufficient to do this.

At the bottom of the cups that constitute the base of the clamps is a piece of felt $\frac{1}{4}$ inch in thickness to prevent the bottles from being broken.

The machine is made in two sizes, for 3 and 12 bottles respectively, by the Denver Fire Clay Company, Denver, Colorado.

The burette attachment shown in Fig. 2 is used in the rapid determination of calcium oxid in lime¹ and consists of a 100 cc. burette (preferably glass cock) having a 5-inch length of $\frac{1}{8}$ -inch glass tubing fastened to the tip by means of a piece of rubber tubing.

The burette is held, by two clamps, to a piece of brass tubing that will slide freely over the $\frac{1}{4}$ -inch rod of a

ring stand and may be placed at any height by adjusting the position of the collar on the rod.

This allows the burette to return to the same position each time a bottle is removed from the clamp.



Fig. 1.

The stopper of the bottle is fitted with a 1-inch length of $\frac{1}{16}$ -inch glass tubing that projects 2 inches below the bottom of the rubber stopper.

Into this the $\frac{1}{8}$ -inch tube of the burette passes.

By this arrangement it is possible to make the titration with the machine running at 300 revolutions

¹ THIS JOURNAL, 2, 10 (1910).

per minute and have none of the solution splash out, at the same time having enough air passing into the

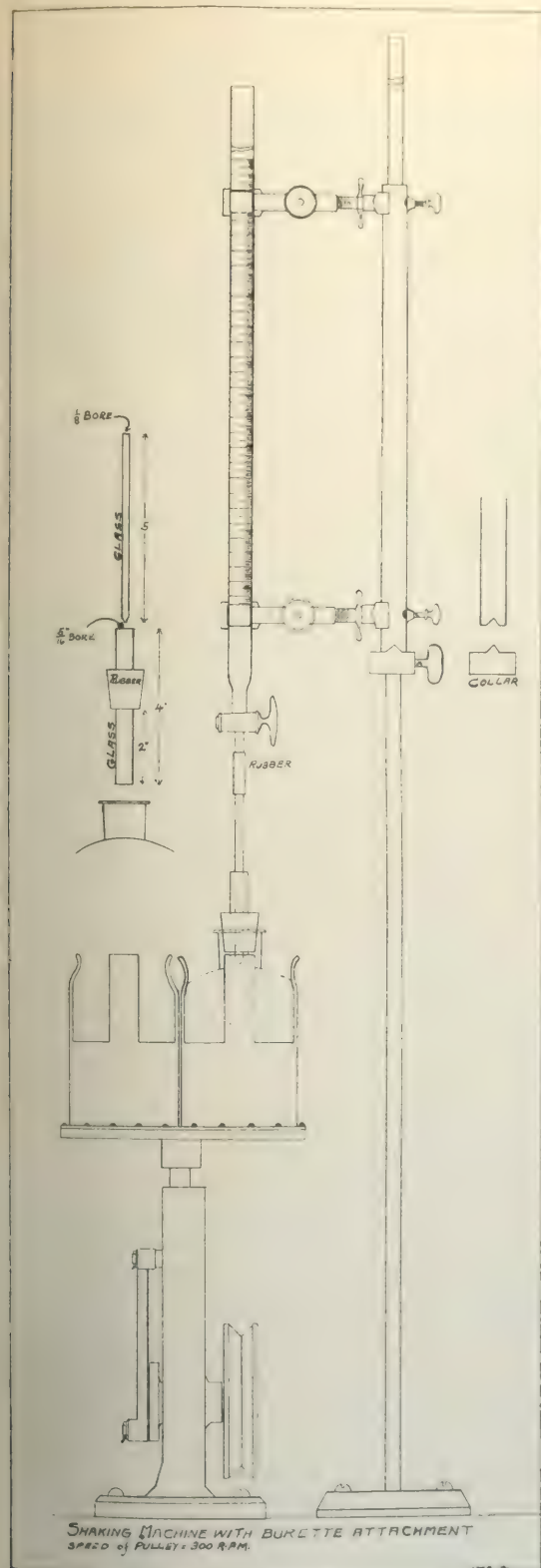


Fig. 2.

bottle to allow the oxalic acid solution to drop freely into the bottle.

STANFORD UNIVERSITY,
May, 1911.

ELECTRIC TUBE FURNACES WITH CALORITE RESISTERS FOR THE LABORATORY.¹

BY ROBERT A. TROTT.

Wire-wound resistance furnaces have now come into general use for electric furnaces in the laboratory and fill a place that perhaps no other heating appliance is capable of.

In our experience we have tried several types of resistors, starting with platinum and some types of chromium-nickel alloys. Platinum, besides being expensive, is not ideal for resistor purposes, as the life is limited and repairs are by no means easy. Nichrome has shown a tendency to crystallize and in this condition breaks under slight strain.

The General Electric Company manufactures a resistance material known as calorite, some of which was kindly furnished to us, and with it several furnaces were constructed which have given great satisfaction.

Calorite is an alloy of nickel, iron, chromium, and manganese, and has a melting point of 1550° C. and a low temperature coefficient. The material as furnished was in the form of tape or ribbon 2.38 mm. (0.094") wide and 0.24 mm. (0.008") thick. It has a resistance of 0.878 ohm per foot and is fairly soft, which is increased by annealing at a low red heat in the air just as platinum wire can be annealed. Oxidation, when heated in the air, is merely superficial even at quite high temperatures, and there seems to be no tendency to crystallize. The alloy cannot be used in contact with silica at high temperatures, and the furnaces were therefore constructed with a view to this property. Three furnaces were made as follows:

No. 1 was designed for tube-heating having a short heating zone which will bring to an even temperature the average size combustion boat. The general construction consists in winding the resistor on a porcelain combustion tube, surrounding it with chemically pure alumina which is held in an asbestos tube and then surrounding the whole with asbestos wool packed between the inside asbestos tube and the outside container which is also of asbestos.

Figs. 1 and 2 are drawings of No. 1 furnace.

A is the porcelain tube of Royal Meissen ware glazed inside, but not on the outside, 457 mm. (18") long with internal diameter of 25.5 mm. (1"), outside diameter 30.5 mm. (1 3/16"). There were collars at

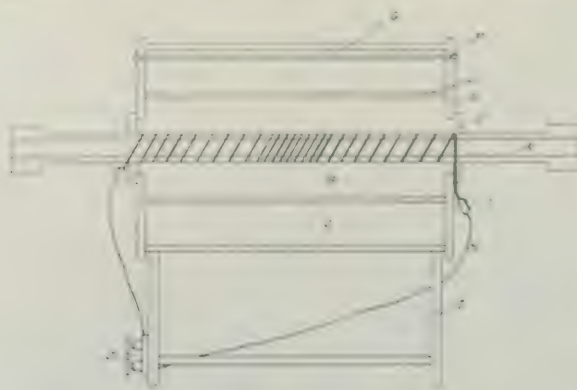


Fig. 1.

¹ Read at the May meeting of the New York Section of the American Chemical Society.

each end of the tube which serve no purpose, but the tube would have been too short had they been removed. These collars had a diameter of 51 mm. ($1\frac{1}{2}$ ") and a length of 25.5 mm. (1"). The tube projected out of the furnace 95.5 mm. ($3\frac{3}{4}$ ") at each end, leaving an available winding space of 267 mm. ($10\frac{1}{2}$ "). This was wound with the calorite ribbon

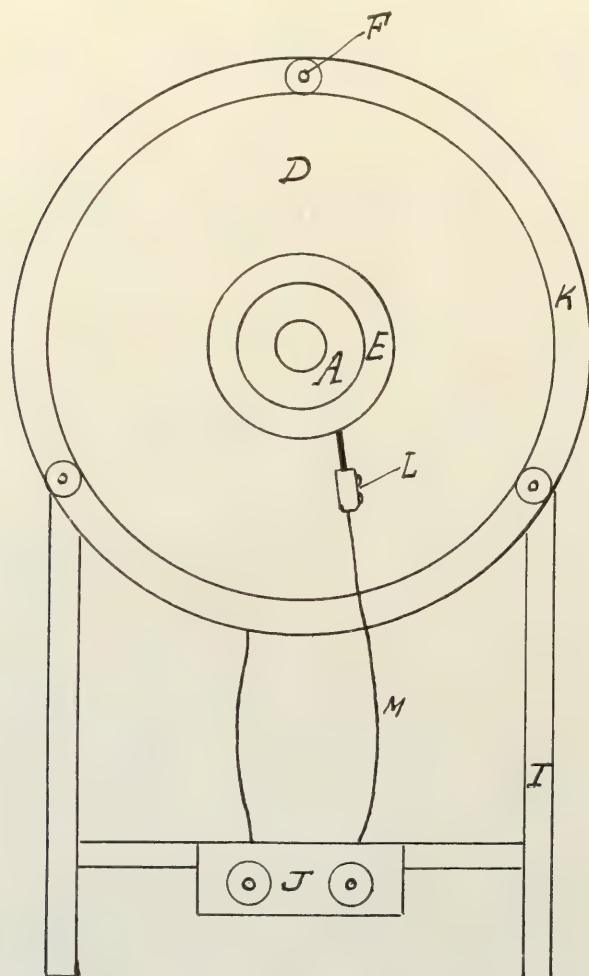


Fig. 2.

taking 28 turns, distributed in 9 turns for the first 108 mm. (4.25 "), 10 turns for the next 51 mm. (2") which is the central portion, and again 9 turns for the remaining 108 mm. ($4\frac{1}{4}$ "). The ends of the ribbon were secured by asbestos cord and sufficient length of the ribbon left for joining with connectors to copper wire leads M.

The end disks D were made of asbestos board 178 mm. (7") diameter, 4.5 mm. ($\frac{3}{16}$ ") thick and were perforated by holes just large enough, 45 mm. ($1\frac{3}{4}$ "), to admit the tube with collar.

Two tubes of asbestos board, G and H, were made, the former 254 mm. (10") long and 165 mm. ($6\frac{1}{2}$ ") in diameter outside, the latter the same length and 89 mm. ($3\frac{1}{2}$ ") diameter. These tubes were made by soaking the asbestos board thoroughly in water and then rolling to the required shape over a bottle or roller and cementing the lapped joints with sodium silicate.

The end-piece D is bored through for the long brass bolts F which hold the end disks tight to the two concentric tubes G and H. The end-disk D are further strengthened by a circular strip of sheet iron, K.

The furnace is assembled by passing one of the disks, D, over the porcelain tube and securing it by means of a split asbestos collar, F, cemented with sodium silicate.

The concentric tubes G and H are next placed symmetrically over the porcelain tube and the interior space B is filled with chemically pure alumina. The outer space C is packed with asbestos wool, the end disk, D, is passed over the tube A and the brass bolts F are drawn up tight. Another split asbestos collar, E, secures the tube A in a central position and the furnace is then assembled.

An iron stand, I, supports the furnace, which is made of light iron, the feet being made of angle iron for greater strength, and was joined up in the open air by an acetylene burner. This iron frame also provides a place for the terminals J in a fiber block, and a permanent electrical connection is made by the wires to the clamps L.

This furnace has a resistance of about 8 ohms and was first operated slowly, using 110 volt direct current, through a variable rheostat. The data of this run are as follows:

Time.	Amperes.	Temperature ° C.
10.00
10.15	5.9	380
10.20	4.6	410
10.40	4.6	550
10.50	4.8	620
11.00	4.8	670
11.00	5.2	..
11.10	5.2	760
11.20	5.2	780
11.20	5.5	..
11.40	5.4	850
11.40	5.9	..
11.50	5.8	960
11.50	6.2	..
12.00	6.15	1030
12.20	6.1	1110
1.00	5.7	1140
1.10	..	1160
1.35	5.4	1140

The voltage increases from 30 at the start to 105 at the end of the run. Temperatures were determined by a thermocouple with the tube closed at both ends, the ends of the porcelain tube being so far away from the heated zone that rubber stoppers can be used. Several other runs were made with this furnace before putting it to general use in the laboratory. The furnace can be easily brought up from room temperature to 770° C. in 30 minutes, using from 4.4 to 9.5 amperes. On another occasion it was kept at 100° C. for the greater part of a day.

No. 2 Furnace is Shown in Fig. 3.—This is designed for crucible work and is made up in the same manner as No. 1.

The calorite ribbon is wound on a portion of large Meissen porcelain tube, A, which was cut from a large combustion tube, giving a length of 102 mm. (4"), including the collar. The inside diameter was 52.5 mm. ($2\frac{1}{16}$ "), the outside diameter being 6 mm.

(2 $\frac{1}{2}$, 38"). Twenty turns of the calorite were wound on the 76.5 mm. (3") space and secured at each end by twisting a piece of the ribbon around the winding,

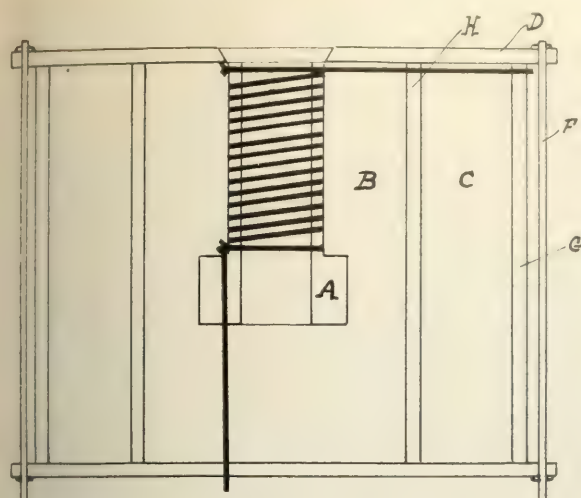


Fig. 3.

as in this case asbestos cord was not permissible on account of the higher temperature to which these portions of the resister are subjected.

The tube is then mounted between the end plates D which hold the concentric tubes of asbestos G and H in position, the filling for space B and C being alumina and asbestos wool as before.

The end plates were of asbestos lumber, which can be easily turned in the lathe and is much stronger than ordinary asbestos mill board. These plates, D, have a diameter of 223 mm. (8 $\frac{3}{4}$ ") and thickness of 6 mm. ($\frac{1}{4}$ "). The outside tube or container is 197 mm. (7 $\frac{3}{4}$ ") diameter, giving space to pass the brass bolts F which clamp the furnace together. The inside tube H is 115 mm. (4 $\frac{1}{2}$ ") diameter, these measurements giving a suitable space, B and C, for the alumina and asbestos wool.

Tube A is closed at the bottom with a porcelain crucible cover which is placed in the tube at the bottom of the resister. This gives a convenient space for crucibles to be heated, which may be of any suitable material. The terminals of the resister are joined to copper wire which is led to binding posts in the end-piece D (not shown). A number of experiments were made in the use of different materials for the tube, such as winding the resister on an ordinary porous cup, but this material does not answer as well as porcelain. Difficulty was anticipated in keeping the resister in place, and various cements were tried. The most successful material for the purpose was found in a cement composed of chemically pure alumina with 10 per cent. phosphoric acid. The use of cement, however, is not to be recommended, and the resister can be kept in position with the aid of the binding clamps of calorite.

The furnace was used on 110 volt density current and gave the following results:

Time	Ampere	Volt	Temperature °C
9 00	4 6	43 0	
10 00	4 48	43 30	360
10 10	4 55	37 5	410
10 30	4 30	38 0	460
10 45	4 58	39 0	510
11 15	4 33	38 0	690
11 40			710
12 00	4 55	37 5	730
12 45	4 55	38 0	750
3 15	4 3	37 00	730
4 00	4 4	38 0	700
4 30	4 6	39 0	700

The furnace was also run more quickly, in 2 hours using 5.3 amperes and 42 volts the temperature reached was 805° C. which could be kept nearly constant.

The furnace is not adapted to quite such high temperature work as the horizontal tube furnaces on account of the thickness of the wall of the porcelain tube and also because the temperatures as taken by the pyrometer are measured in the open space, thus the temperature of the resister must be very much higher than at the thermocouple junction, the difference being much greater than in the case of the horizontal furnace. 800° C. is about the maximum temperature that it is safe to use with this type of furnace.

Another horizontal tube furnace was built similar to No. 1 for heating a greater length of the porcelain tube. The inside diameter of the tube is 19 mm. ($\frac{3}{4}$ ") and the total length 610 mm. (24"). Allowing 153 mm. (6") to project at each end gives a winding space of 305 mm. (12").

This was wound as shown in Fig. 4 with 8 turns of the calorite in 38 mm. (1 $\frac{1}{2}$ "), 25 turns in the middle portions of 228 mm. (9") and 8 turns at the other end-space of 38 mm. (4 $\frac{1}{2}$ "). The object here is to heat the tubes as evenly as possible throughout a length of 305 mm. (12"), and this is accomplished by

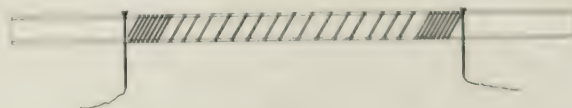


Fig. 4

increasing the number of turns of the resister at the ends where the heat losses are greatest. The general dimensions of the furnace are nearly the same as for No. 1, except for the somewhat greater length of tube. In this furnace asbestos lumber was used for the end-pieces D and the resister was held at the ends with calorite clamps.

Time	Ampere	Volt	Temperature °C
10 23	5.3	43 0	
10 28	5.05	44 3	300
10 48	5.08	46 0	715
11 10	5.2	47 5	900
11 30			970
11 40			980
11 55			1010
11 55	4 75	46 0	
12 03	4 72	45 0	1000
1 10			970
2 45	4 55	45 5	935
4 00	4 5	46 5	940
4 20			1050

The run with this furnace to try it out is given in the preceding data.

With care the temperature may be maintained constant at 1000° C. This has been done with No. 1

furnace in many experiments in which a boat was kept at a temperature of 925° C. for several hours.

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ADDRESSES.

THE EARNING POWER OF CHEMISTRY.¹

By ARTHUR D. LITTLE.

Received July 11, 1911.

It may fairly be claimed for chemistry that it is at once the most fundamental and the most comprehensive of all the sciences. Its province, in the classical definition of Ostwald, is "The study of the different forms of matter, their properties, and the changes which they undergo." Thus defined, chemistry embraces the material universe, our solar system, the most distant stars and the flaming nebulae no less than the dust speck within the universe, on which we live and which we call the earth. It includes within its subject matter the physical basis of our own bodies and of those of every living thing upon the earth. It is directly concerned with the air we breathe, the water we drink, the food we eat, the materials upon which we expend our labor, and the things which we buy and sell.

To me has been assigned the pleasant task of bringing home to you some conception of the extent to which you are already indebted to this science and a better appreciation of the comprehensive benefits which it still holds out to you.

The world in which we live is a different world to every individual in it, as it has been a different world to every generation of the race of men. To no other generation have its confines been so opened out and broadened as to our own. To the man congenitally blind, tapping his way along the curb, a modern city is a place of sounds and measured spaces; to one who sees, it becomes a world of light and movement and ever-changing shades. Plymouth Rock is a very ordinary piece of granite to one who knows not its history; to the better informed it stands as the symbol of that adventurous spirit and uncompromising virtue on which the foundations of our country rest. To the world at large coal-tar is a black and evil-smelling nuisance; to the eye of the chemist it is replete with all the potentialities of the rainbow.

So it happens that the world as viewed by the chemist presents an aspect different in many ways from that in which it appears to the mind not chemically trained. As the astronomer perceives in the movements of the stars a relationship and coördination to which the average man is blind, and deduces from them generalizations by which both the intellectual and practical life of the community are profoundly influenced, so the chemist, who may be regarded as the astronomer of the infinitely minute, studies the movements and interchange of atoms and the structure of the molecular systems which result therefrom. In other words, the astronomer

interprets the universe in terms of certain units, which are the heavenly bodies, while the chemist seeks his interpretation in terms of the ultimate particles of which matter is composed, whether they be molecules, atoms, ions or electrons. And, since the different forms of matter, in their flux and flow, together constitute the universe, the properties of matter and the changes which these properties undergo are of compelling interest and importance to each one of us in every activity of our lives.

We live immersed in an ocean of air and we draw this air into our lungs approximately eighteen times a minute. The quality of this air, its temperature, pressure, humidity, the minute impurities which may be present, affect our comfort and well-being in many ways. It supports the chemical processes of combustion by which our existence is maintained no less than those upon which we are chiefly dependent for light and heat and power. The nature of this all-enveloping atmosphere of air has always been a subject of speculation, though to little purpose before the advent of chemistry.

Modern chemistry had its birth in the eighteenth century study of the air and its relation to the processes of respiration and combustion. Prof. Ramsay has said that "To tell the story of the development of men's ideas regarding the nature of atmospheric air is in great part to write a history of chemistry and physics." The story is one which has reached its culminating interest in our own most recent times. For \$35 you may now buy apparatus for reducing air to the liquid form and study the properties of matter at temperatures nearly as low as that of interstellar space.

Within the memory of the youngest undergraduate in chemistry the brilliant researches of Ramsay, Raleigh and other chemists have disclosed the presence in the air we breathe of five new gases of remarkable and in some respects unique properties. To one of these, neon, we now confidently attribute the long mysterious phenomena of the aurora borealis. Tubes containing highly rarefied neon may become as commonplace to our descendants as candles were to our forefathers. They glow with a rich, mellow, golden light on the passage through them of an electrical discharge.

The heavy toll of life in mine disasters would be unsupportably heavier were it not for the Davy lamp, the fire-damp indicators, the rescue outfits and the regulation of explosives, all of which have become possible only through the growth of chemical knowledge. Ventilating systems as applied to theatres, halls and dwellings are based on chemical studies of the rates and causes of increase in the carbonic acid

¹ A public lecture to business men delivered June 29, 1911, under the auspices of the Indiana Section of the American Chemical Society.

content in the air of rooms. The proportion of sulphur permissible by law in illuminating gas finds its justification in similar studies on the air in rooms in which such sulphur-bearing gas is burned.

The chemical and biological study of public water supplies, which received its first systematic development little more than twenty years ago at the hands of Drown and Mrs. Richards in the laboratories of the Massachusetts Institute of Technology, has been the means of saving countless lives throughout the world and has led to such understanding and made possible such control of sources of pollution as to almost justify the statement that for every case of typhoid fever some one should be hanged. Chemistry can now determine in advance of use the suitability of a given water supply for use in boilers or for the requirements of any special line of industry, as paper-making, dyeing, cloth finishing, brewing and so on. Furthermore it supplies the means for correcting undesirable characteristics in a water supply as by use of filtration apparatus, coagulants, water-softening systems and the Moore method for the destruction of the algae which in many waters are the cause of unpleasant tastes and odors.

Nowhere is the practical value of chemistry in its relation to the affairs of every-day life more strikingly demonstrated than in connection with our food supply. Chemical fertilizers are in large and constantly increasing measure responsible for the enormous total of our agricultural products. The whole fertilizer business is under the strictest chemical control, and the farmer buys his fertilizer on the basis of a knowledge of its composition and effective value which puts the average purchasing agent of a manufacturing company or public service corporation to shame. The Association of Official Agricultural Chemists, and the laboratories of the agricultural colleges and experiment stations throughout the country are doing more to keep down the cost of living than all the lawmakers we send to state capitols and Washington.

One of the most insistent of the demands of growing plants is that for nitrogen in form available for plant food. A small proportion of the necessary supply of nitrogen in the assimilative form is derived from the manure of farm animals and from animal wastes of various kinds, but for many years the world has depended upon the nitrate beds of Chili as the chief source of this indispensable element of plant growth. It is bad enough to be tied in this way to a single far-away deposit, but the situation becomes alarming when we discover that this deposit can hardly meet the world's demand for nitrate for another twenty years. One may contemplate the Malthusian theory with indifference or even with disbelief, but here is a condition not to be gainsaid. The world must do something to meet it within twenty years or the world must make up its mind to starve. Fortunately for the world the chemists are already doing something. They have recognized that 33,800 tons of nitrogen are pressing down upon every acre of land and have boldly attacked the problem of rendering available such portion of this inexhaustible supply as the world

may need. The methods employed have been daring and brilliant in the extreme.

In 1785 Cavendish in a paper before the Royal Society describes the production of nitric acid by the passage of an electric spark through air. A hundred years later Bradley and Lovejoy at Niagara Falls, by drawing air through an apparatus by which 400,000 arcs were made and broken each minute, demonstrated the possibility of the commercial manufacture of nitrates from atmospheric air. Birkeland and Eyde in Norway pass the air through furnaces in which it comes in contact with enormous flaming and rotating arcs. Rossi in Italy brings the air in contact with highly incandescent material of special composition. Although by these several processes nitrate has been produced by thousands of tons it is doubtful if the artificial product can yet compete with Chilian. Even now, however, the margin is not a wide one and the results already accomplished amply prove that when our agriculture begins to feel the pinch of a failing nitrate supply the chemist may safely be relied on to meet the situation. This assurance is rendered doubly sure by the fact that a solution of the problem along altogether different lines is already nearly or quite within our hands. Dr. Frank has shown that by heating calcium carbide, itself a comparatively recent product of the laboratory, in a stream of nitrogen there is formed a new compound, calcium cyanamide. The practical interest in this compound depends upon the fact that when exposed to a current of steam it decomposes into ammonia and carbonate of lime and that the same reaction takes place slowly in the soil when the cyanamide is mixed therewith. Since the nitrogen in ammonia is directly assimilable by plants and since calcium carbide requires for its production only lime and coke and power we may view without serious concern the approaching failure of the Chilian nitrate beds.

But it is not only on the side of agriculture that chemistry touches our food supply. Chemistry pervades the packing industry, reducing the cost of food by utilization of by-products of the most varied character from oleomargarine to glycerine and soap and from soap to pepsin and adrenalin. To Atwater and his co-workers we owe our knowledge of the energy-producing value of different foods in the human economy and to Wiley and those other chemists behind him on the firing line we are indebted for the far-reaching benefits of the Pure Food Law.

Carbon disulphid made in the Taylor electric furnace has preserved the wine industry of France by destroying the phylloxera as it is ridding our own fields of prairie dogs and our elevators of rats and mice. Bread-making and brewing are coming each year more and more within the recognized domain of chemistry which is at the same time greatly enhancing the value of our staple crop by the increasing production of glucose, corn oil and gluten. Exactly one hundred years ago Kirchhof discovered the inversion of starch to glucose by dilute acids. To-day the United States alone is richer by \$30,000,000 a year by reason of that discovery.

The relation of chemistry to the clothes we wear is perhaps less obvious but still of the first importance. More land is planted to cotton and cotton itself is cheaper because chemistry has taught the planter how to secure increased yields by proper fertilization and how to obtain increased profits by utilization of the cottonseed for oil and cattle feed. Chemistry is even now developing new sources of profit for the planter by adapting the short fiber adhering to the ginned cottonseed hull to the making of smokeless powder and the stalks of the cotton plant to paper-making.

The woolen industries are dependent upon chemistry for the processes of separating the pure fiber from the grease and dirt with which it is associated in the raw wool and for the methods of working up this wool waste into oleic acid, soap, lubricating oils and potash and ammonia salts, as well as for the process of carbonizing by which the wool is separated from the burrs and other vegetable material with which it is admixed in the fleece.

Many of the most brilliant achievements of chemistry have been directly concerned with the textile industries. A little touch of chemistry to cotton yarns and fabrics in the mercerizing process gave the world what is practically a new textile fiber—cotton with the beauty and luster of silk. A history of absorbing interest replete with struggle, the capture of positions of temporary advantage, the constant shifting of the fighting line, crushing defeats and signal victories might be written of the development of the bleach and alkali industry, upon the products of which the textile manufacturer depends for the finishing of his goods. We see the pathetic figure of Le Blanc dying in the poorhouse after enriching the world which Napoleon was devastating. No less interesting in its human and scientific aspects is the long story of the coal-tar colors in which chemists take so large a measure of justifiable pride. An investment of \$750,000,000 follows Perkin's discovery of mauve.

Less notable, but nevertheless an industrial achievement of the highest order is the very modern development of artificial silk which, though made from wood pulp, far surpasses in brilliance and beauty the finest product of China and Japan. Closely related, thereto, is the artificial horsehair of which so large a proportion of women's hats are made and the still more recent artificial bristles of cellulose acetate with which you may have brushed your hair this morning.

A complex series of chemical reactions has its origin in the striking of every match, and civilization as we know it could hardly exist without the modern facilities for securing artificial light. For the extraordinary extension of these facilities during the past century the chemist has mainly been responsible. The immortal Faraday selected "The Chemistry of a Candle" as the subject matter of a classical series of lectures to audiences of children. From the rush candle and the tallow dip to the candles of stearin and paraffin is in itself a long journey, the milestones on which were set by Scheele, Chevreul, Heintz and Tilghman.

The refining of petroleum involved the solution of many difficult chemical problems. The Chicago fire is said to have been started by Mrs. O'Leary's cow which kicked over a kerosene lamp. In those days, however, it was not necessary to invoke the cow to start a conflagration with kerosene. Much of the lighting oil upon the market at that time would flash below 100° F. We owe our present safety in the use of kerosene largely to the work of Prof. Chandler.

The production of illuminating gas is wholly a chemical process. When coal gas was first employed for lighting the Houses of Parliament the members might be seen gingerly touching the pipes to discover if they were not indeed hot from carrying such flame. That gas is now so cheap is due in large part to the development by Lowe of the chemical process for making water gas by passing steam through a bed of glowing coals and to the chemical processes for gas enrichment. By the Blaugas system illuminating gas is now produced in liquid form and distributed in steel bottles to isolated consumers like so much kerosene.

The gas mantle by which the illuminating power of gas is raised from 16 to 60 candles on a consumption of 3½ feet an hour constitutes one of the most significant triumphs of chemical research. Certain sands found in Brazil and known as monazite sands had long been a happy hunting ground for chemists by reason of the number of rare metallic elements to be found therein. They seemed to be a sort of chemical garret where everything not otherwise used up during the process of creation had been stowed. Dr. Carl von Welsbach was investigating the rare elements in these sands some thirty years ago and studying their spectra. It occurred to him that a better flame for his purpose or rather a better distribution of the metallic vapor in the ordinary Bunsen flame might be secured by distributing the metallic compound through the substance of a bit of cambric. He dipped the cambric in a solution of the salts, suspended it in the flame, burned off the cotton, and found that the fragile gauze glowed with an amazing brilliance. So came into being the gas mantle which has revolutionized and saved the illuminating gas industry, though not until the initial discovery had been followed by years of the most painstaking and refined research.

In the development of electric lighting the chemist has played a part scarcely less important than that of the electrician.

The arc light was first shown by Davy between charcoal points and was maintained by the current developed by the action of chemicals in the enormous battery of the Royal Institution. To Faraday, whose achievements in electricity have overshadowed his renown as a chemist, we owe the discoveries upon which our modern methods of generating electricity are based. The early history of the incandescent lamp is a chronicle in equal measure of the difficulties of finding a proper material for the filament and those of producing the requisite degree of vacuum in the bulb. Both problems were solved by chemistry which first supplied the carbon filament made by dissolving cellulose, squirting the solution into a

thread of the required diameter, drying and carbonizing the thread and thereafter flashing in an atmosphere of hydrocarbon vapor to deposit carbon on the filament precisely where and in exactly what proportion its original inequalities of resistance to the current made necessary. More recently Whitney and other chemists working in the same field first greatly raised the efficiency of the filament by the process of metallizing, so-called, and have since given us lamps of an altogether new order of usefulness by employing new materials, as tungsten, for the filament.

The second great problem, that of securing rapidly and cheaply the necessary high vacuum in the bulb, was solved in the most elegant manner by the extraordinary Malignani process. Malignani placed within the tubulature leading from the bulb and connecting the bulb and pump, a minute quantity of red phosphorus, started the pump and roughly exhausted to about 2 mm. of mercury. He then sent through the filament a current so heavy as to bring the filament to intensive incandescence and cause the gaseous residue within the bulb to faintly glow so that the bulb was filled with a luminous blue haze. He then sealed off the pump by fusion of the walls of the tubulature below the phosphorus and with the bulb still glowing touched the tip of the blowpipe flame to that portion of the tubulature wall against which the phosphorus rested. With the vaporization of the phosphorus the blue haze instantaneously disappeared and an almost perfect vacuum was secured within the bulb. The process is not one of oxygen combustion as might on first thought appear and its ultimate mechanism was not understood until many years subsequent to its discovery.

The improvements in incandescent lamps in the last ten years have resulted in the saving of \$24,000,000 a year in the cost of lighting as compared with the cost of equal illumination by the older types of lamp.

To the art of illumination Wohler and Willson have contributed the calcium carbide and acetylene found on every automobile and in a hundred thousand isolated homes; Pintsch and Blau have developed separate systems permitting the transport of illuminating gases in steel tanks for the lighting of trains and houses; to Hewitt we owe the mercury lamp, to other inventors the flaming arc, to Nernst the high efficiency lamp which has his name, and, long before them all, to Bunsen the blue flame burner utilized by Welsbach and which constitutes the basic element in every gas stove.

I have endeavored in this cursory and most inadequate survey to indicate something of the extent to which chemistry contributes to the satisfaction of the demands and needs of every-day life. The earning power of the science becomes more directly apparent in its relation to general industry.

American manufacturing is in many respects the most intensive in the world. Nowhere is plant scrapped so quickly to be replaced by larger, faster and more efficient machines. Nowhere else is labor so speeded up by piece work, bonuses, motion studies,

gang organization and the other devices of the efficiency engineer. In no country can new office systems, typewriters, adding machines, time recorders, memory ticklers, duplicating devices and all the paraphernalia of the follow-up be sold as quickly and in none are they utilized so thoroughly. Our manufacturers understand these things, and what they understand they want, and are quick to make the most of, provided always they can use it in their business. They do not understand chemistry, naturally they do not propose to have any chemist teach them their business. This is reflected in the attitude of their subordinates which is commonly one of militant skepticism. They, like their masters, cut themselves off from that great coördinated and organized body of knowledge brought together by thousands of highly trained minds through the incessant questioning of nature during a hundred years. They pay less regard to many of the laws of nature than they do to city ordinances. When under these circumstances they fail to make a satisfactory profit in competition with more enlightened Germany, they jack up the tariff. They ignore applied chemistry which offers them better protection than the highest schedules of the Aldrich bill.

Let us consider a few concrete examples of the earning power of chemistry. A large pulp mill found itself with over 100,000 cords of peeled wood piled in its yard and this wood was beginning to rot. A few thousand gallons of sulphite liquor sprayed over the pile from a garden hose killed the fungus and saved the pile. The same mill was losing 23 per cent. of its wood as barker waste. Laboratory trials proved that an excellent quality of paper could be made from this waste, all of which in this mill is now profitably worked up. Other mills still throw 20 per cent. or more of their initial raw material away. The mill was cooking in 16 hours. Laboratory cooks were made in 7½ hours and the time of the mill cook reduced to 10. Finally, by a proper spacing of the digesters, the production of the plant was brought from 97 tons a day to 149 tons.

Cylinder oils generally cost about what you are accustomed to pay. Plants which employ a chemist pay from 19-27 cents. Manufacturers who do not need a chemist commonly pay 45 cents, 65 cents or even, if they know their own business very well, \$1.50 a gallon. There is probably not a large plant in the country in which, if it is not already under chemical control, the lubrication account cannot be cut in two. In the engine room of one large cement plant the average monthly cost for lubricants had been \$337. It is now \$30. A concern paying 37 cents a pound for a special grease which the superintendent needed to run the mill now buys on specification for 5½, and the mill still runs. Another company within our knowledge saves \$12,000 a year on cutting oils alone.

In a plant near Boston using two tons a week of special steel rolled very thin, their chemist was able in about two years to reduce the cost of the material from 80-40 cents a pound while at the same time standardizing and greatly improving the quality of

the steel. We recall savings of \$2,100 a year on wrapping paper, \$3,600 on boiler compounds, \$6,800 on a minor article of supply, \$100,000 a year on a single raw material. Prof. Duncan in his fascinating and suggestive book, "The Chemistry of Commerce," says: "On three separate occasions the writer has visited the same glass house to see the workmen bailing out a lake of violet spoiled glass from the same immense tank, and all because it was deemed by the foreman 'theoretical' to have the manganese analyzed in order that its quality might be adjusted to its oxidizing value. Thousands of dollars were thus wasted and thousands more lost through failure of the firm to fulfil its contracts on time, and all of it could have been saved at the cost of, say, \$10 for a simple analysis."

Chemistry points out the only proper way to buy supplies which is on the basis of their industrial efficiency by means of specifications defining the quality desired and rigid tests to make sure that quality is secured. Independent estimates by those in exceptional positions to know place the efficiency value of supplies as purchased and used by American manufacturers at 60 per cent. of what it should be.

Comparatively few American manufacturers light their cigars with \$20 bills. It is too slow a method of burning money. They prefer to burn it by shovelfuls, so they burn it in the boiler room. They forget that in ostensibly buying coal they are really buying heat and they pay good money for slate and sulphur balls with no knowledge of the actual number of British thermal units they are receiving for a dollar. Perhaps they depend upon a trade name ignoring the fact that coals from different mines in the same district vary greatly as does also coal from the same mine. Moreover coal, like some other things, is not always true to name. A few years ago the Boston School Committee decided to buy its coal on specification. It had previously bought "New River coal of the best quality" and that definition of its desires was included in the specification which, however, also included a chemical definition of what coal bearing this name should be. When deliveries were made by the same dealer who had previously supplied school coal they proved to be an inferior grade of Pennsylvania coal with sulphur in some samples running up to 6 per cent. When the contractor was called to account, he admitted that he did not know the state in which New River coal originates nor the transportation route by which only it could come to Boston. His comment to the committee was, "I don't see what you are fussing about, it's the same coal you've always had." Later when the temperature in the piles in a certain school ran up 90° in one day he was called upon to remove all coal delivered by him to schools in that district and substitute therefor New River coal, which he did at heavy loss to himself and corresponding gain to the city.

Important as are the losses in the initial purchase of coal, they are small compared with those which attend its burning. Many a mill owner looks out of the window and sees, without knowing, his dividends

go up the chimney. Under well regulated conditions of combustion the flue gases should contain not less than 12 per cent. of carbonic acid gas. They frequently contain no more than 3 per cent. This means that for every ton of coal burned under the latter conditions more than 52 tons of excess air are heated to the high temperature of the flue gases. Chemistry meets these conditions by analyzing the flue gases and regulating the draft as indicated by the percentage of carbonic acid found. At \$2.25 a ton, which is much below the average price, the fuel bill of the United States was over \$1,000,000,000 in 1910. Of that amount chemistry could easily have saved \$100,000,000.

Chemistry aids the manufacturer who will listen to her teachings in countless other ways. It substitutes a rigid control of processes for the guesswork and uncertainty of the rule of thumb. It increases the productivity of labor by supplying more efficient processes.

In the sulphur mines of Sicily young boys called *carusi* climb with groans and curses for four hundred feet bearing in a stifling atmosphere 40 pound loads of sulphur ore upon their backs. In Louisiana, thanks to Frash, two concentric pipes are driven to the ore, a hot solution of calcium chloride is forced through one pipe to melt the sulphur which is then pumped to the surface through the other, at a trivial fraction of the cost of raising the ore in Sicily.

In the old days of making paper the rags were piled in a heap, moistened and allowed to stand for weeks until fermentation had proceeded far enough to soften them. Now they are boiled with lime for a few hours. They used to be bleached by the slow action of the sun and dew as they were spread upon the grass. They are brought to better color now over night by bleaching-powder. Cutting tools made from high-speed steels multiply the output of the lathe and planer. The addition of 1 per cent. of calcium chloride to the electrolyzing bath doubles the yield of potassium chlorate.

Chemistry aids the manufacturer by standardizing his product and reducing seconds and rejections. It costs just as much to tan goat skins into seconds as into firsts though seconds bring a third as much. Chemistry even comes to the front bearing ammunition during an advertising campaign. You may remember the offer of a blowpipe and a bit of charcoal coupled with the information that if your paint was a lead paint as the advertiser believed it should be you could quickly prove its quality in the laboratory of your kitchen by reducing from the paint a little pellet of metallic lead. You do not see that advertisement now. It disappeared about the time that some one else informed the world that zinc paints are "unalterable even under the blowpipe."

Nowhere, however, does chemistry render such efficient service to the manufacturer as in turning to profit waste and nuisance. To this phase of its service we shall return again.

To quote once more Prof. Duncan:

"During the next five years the small manufacturer

who is swept out of existence will often wonder why. He will ascribe it to the economy of large scale operations, or business intrigues or what not, never knowing that his disaster was due to the application of pure science that the trust organizations and large manufacturers are already beginning to appreciate."

A few of us have been surprised, and none more than the railway managers themselves, by the well supported statement before the Interstate Commerce Commission that the railroads of the country could save \$300,000,000 a year by the application of scientific management to the operation of their properties. Every chemist who has studied the problem is well aware that the entire amount in question could be saved through utilization of the proved results of chemistry alone.

Abraham S. Hewitt is authority for the statement that the Bessemer process has added \$2,000,000,000 yearly to the world's wealth. By far the greatest portion of this increment has come through the economies which this process of steel-making has rendered possible in transportation.

Our own study of car painting practice on 21 electric roads has developed the fact that 50 per cent. of the cost of materials and labor is wasted and more than 50 per cent. of the time spent by the cars in the shops is unnecessary.

The classic work of Dr. Dudley as the head of the laboratories of the Pennsylvania system has gone far to standardize railroad practice throughout the country. Few even among railroad men realize how greatly the whole community is in his debt. His specifications cover rails, soaps, disinfectants, oils for signals and for lubricating, paints, steel in special forms for every use, car wheels, cement, signal cord and every detail of equipment. He has made the transportation of life and property cheaper, safer and more expeditious by reason of his application of chemistry to the problems of railroad management.

In a recent address Dr. Frankforter, voicing the opinion of every thoughtful chemist, said: "The United States is the most wasteful nation in the world; wasteful in living, wasteful in manufacturing, and wasteful in conserving its natural resources." So heedless and appalling is this waste that the mind trained in chemistry stands aghast. I have lately visited a southern lumber mill which burns 1,900 cords of wood a day in its incinerator. There are two hundred such burners in the country limited in destructiveness only by the amount of material sent to them. From such wood chemistry is prepared to extract three gallons of turpentine a cord, 10 gallons of ethyl alcohol, or paper pulp to the value of \$20. We waste each year 500,000,000 tons of coal and each day a billion feet of natural gas. With peat deposits fringing our entire eastern coast we pay \$4 a ton for coal delivered on the bog. Beehive coke ovens flame for miles in Pennsylvania and excite no comment while the burning of a \$1,000 house would draw a mob. We fill the Merrimac River with wool grease making it a stench, while the towns along its course buy soap and fertilizer and lubricants from Chicago,

Chili and Pennsylvania. We burn coal-tar in Massachusetts and import coal-tar colors at high prices from Germany. Over the great northwest we burn each year 5,000,000 tons of flax straw while we pay \$40 a ton for imported paper stock from Norway. In the South 300,000 tons of paper fiber of the highest grade are burned with the cottonseed hulls to which it is attached or used with them to adulterate cattle feed. Corn-stalks to an incalculable tonnage rot or are burned each year while chemistry stands ready to convert them into feed containing 30 per cent. of sugars on the dry basis, or into alcohol for light and power. Waste molasses is sold for three cents a gallon or dumped into the stream while alcohol sells for 40 cents a gallon. Skim milk is fed to hogs or thrown away because no one has the enterprise to extract its casein which is worth more than beefsteak for food.

In the face of such conditions we still meet young men who would inform us that the day of opportunity is past. The truth is that opportunity is knocking not once but insistently and long at every entrance to the chemist's laboratory.

Nowhere is the earning power of chemistry better shown than in its ability to transform cheap raw materials into products of exceptional value. A cord of wood is worth perhaps \$10 with a dry weight of a little over a ton. Its value, therefore, is about a half a cent a pound. In the form of chemical fiber for paper-making half the weight is lost but the remainder is worth $2\frac{1}{4}$ cents a pound. As paper it finds a market at 4 cents. Made into artificial silk by more refined chemical processes it commands \$2.00 a pound, while as cellulose acetate bristles it is worth \$4.00.

Many of our great industries are founded on minute chemical facts. Goodyear drops a bit of gum mixed with sulphur on a hot stove and the rubber industry results. The fact that silver salts happen to blacken when exposed to light is responsible for a corporation with \$35,000,000 capital on which the earnings are over 20 per cent. a year. The dipping of cotton yarn in caustic soda while tightly stretched has revolutionized the manufacture of the better grades of cotton textiles. Because the chemist learns that glycerine treated with nitric acid becomes explosive our army engineers are able to separate two continents. Becquerel, having placed a bit of uranium upon a photographic plate in a black paper wrapper, finds on development that the plate has blurred. The observation leads Prof. and Madame Curie to study similar actions by uranium ores and presently the thought of the world is enriched by altogether new conceptions of the constitution of matter, and our minds are awed by the magnitude of forces previously unrecognized.

Two classes of securities find a ready sale in Massachusetts— $3\frac{1}{2}$ per cent. bonds and gold bricks. It is not an easy matter to raise money for a sound chemical proposition which promises 20 per cent. Much the same conditions undoubtedly prevail throughout the country. Boston, which invested largely in sea water

gold, the Hickman machine for converting starch to cane sugar, and the electrical process by which spruce wood was transformed into Australian wool with the grease in and the burrs attached, is just now figuring its losses on synthetic rubber. It left to other communities the formula of the Altoona cobbler for burning ashes, the process for converting water into kerosene, and the Lamoine diamonds. Men who turn a box of strawberries upside down and require a pastor's certificate of character from the office boy, rush into misapplied chemistry with never a thought of expert investigation or advice. The pity is the greater when one realizes, as every chemist does, the generous scale by which are measured the rewards of chemistry properly applied and wisely administered. Ten years ago a Massachusetts company with a capital of \$20,000 was organized to conduct a manufacture based on chemistry; two years ago it charged off \$700,000 on real estate and equipment; to-day it has a surplus of over \$1,000,000. The great Badische Anilin und Soda Fabrik, the Elberfeld Co., Brunner, Mond & Co., the E. I. duPont de Nemours Powder Co., Meister, Lucius & Bruning, the Solvay Process Co., and many others well-known to every chemist are among the most profitable industrial organizations in the world. The one thing lacking for an enormous development in this country of equally profitable enterprises based on chemistry is a reasonable appreciation by our business men of the earning power of chemistry.

The ordinary investor who may safely trust his own judgment in matters involving cotton, wheat, mortgages, railroad shares or telephones is not equipped by training or experience to decide upon the validity of propositions involving chemistry. He must, if he would avoid disaster, rely upon the opinion of disinterested experts. Such opinion should cover the soundness of the chemistry involved, the state of the art relating to the manufacture, the patent situation, the available market, the nature and extent of competition, the supply of raw material, the stage of development of the process, the cost of plant and the costs of production. These last should be itemized and the basis for conclusions regarding every item should be fully stated. Large allowances should invariably be made for depreciation and in most cases equally liberal allowances for contingencies. Secret processes should be left to the fool and his money.

In this environment and on this occasion I cannot forbear making a brief concluding reference to that organization of chemists which now enjoys your hospitality. At Northumberland, Pa., there lies the body of an obscure English dissenting clergyman who went through life on a salary of £30 a year, although he had enriched the world by the discovery of oxygen. It was around the grave of Priestley on July 31, 1874, that the idea of the American Chemical Society first took form in the minds, and may I add the hearts, of a few American chemists met to do honor to his memory. Subsequent meetings were held in New York at the home of that Nestor among American chemists, Prof. Charles F. Chandler until on April 20, 1876, the Society was formally organized. From

a feeble organization of distinctly local character, with only 200 members in 1887 it has through the service and self-sacrifice of a long series of devoted officers become the largest chemical society in the world, with 5,500 members, and is to-day the most powerful influence in America for the advancement of chemical science. Its claim upon the loyalty and support of every American chemist can no longer be denied or set aside. With equal justification it may appeal to the whole community for recognition and encouragement.

There are in the country at least 100,000 doctors and nearly 125,000 lawyers. There are only 10,000 chemists to carry on a work incomparably more important than litigation and no less beneficial than medicine to the life of the community if that life is to be worth living. Some measure of the mere material benefits which chemistry can offer may be found in the fact that the annual production of the chemical industries of the United States is already nearly equal in value to our agricultural products. Let us, however, not forget that these benefits have come, as many more will follow, because chemists have never faltered in pursuing truth for years through the labyrinth of difficult researches with no better guide than the slender and often broken thread of an hypothesis. Turgot has said: "What I admire in Christopher Columbus is not that he discovered the new world but that he went to look for it on the faith of an idea."

THE UTILIZATION OF THE WASTES OF A BLAST FURNACE.¹

By EDWARD M. HAGAR, President, Universal Portland Cement Co., Chicago.

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Until the last decade, practically the only utilization of the wastes or by-products of a blast furnace was the use of a portion of the waste gases to raise the temperature of the incoming blast through heating the brick work in so-called hot stoves, and in some cases a small portion of the power value of the gases was obtained by burning them under boilers to generate steam for driving the blowing engines.

At the present time the calorific value of the waste gases is being utilized directly in gas engines for blowing purposes and for generation of electric power, a considerable portion of the slag is used in the manufacture of Portland cement, and the flue dust, consisting of the finest ore and coke particles, is being collected and converted so as to be rechargeable into the furnaces.

The aggregate saving or profits resulting from these three developments is a matter of millions of dollars per annum, and in a modern blast furnace plant, it would almost seem that pig iron was the by-product; and, indeed, the investment in the equipment to utilize these former wastes exceeds that of the blast furnace itself.

The writer, in his work, has come in contact with

¹ Presented before the Congress of Technology at the Fiftieth Anniversary of the granting of the charter of the Massachusetts Institute of Technology.

these evolutions, with plants in operation, or under construction, of a capacity to produce twelve million barrels of Portland cement per annum from slag and limestone, using over one million three hundred thousand tons of slag in a year, these plants being driven entirely by electric current generated by gas engines directly from the waste blast-furnace gases, the power requirements being forty thousand horse power for twenty-four hours every working day. In one of the cement plants the first commercial method for reclaiming flue dust was discovered.

By using the blast-furnace gases directly in combustion engines, after suitable washing to remove the grit, the power obtained from a given amount of gas is equal to at least two and one-half times that obtainable by burning the gas under boilers for generating in steam engines.

A modern blast furnace of the usual size, with gas blowing engines, and gas engines driving electric generators, will provide sufficient gas to furnish seven thousand kilowatts electric power, in addition to driving its own blowing engines.

This permits the most modern steel works, such as those at Gary, Indiana, to practically do away with the use of coal for power purposes, operating the rolling mills by electric power from the surplus gases.

The United States Steel Corporation, of which the Universal Portland Cement Co. is a subsidiary, has already installed two hundred and fifty thousand horse power gas blowing and gas electric units, which, it can easily be figured, displaces or saves the consumption of approximately a million tons of coal per annum as compared to the old-fashioned method.

With the modern high blast pressures, and the use of fine Mesaba ore, the finest of the particles, together with the coke dust, are blown out through the top of the furnaces and are caught in the flues, dust catchers and gas washers.

The iron ore in this dust amounts to fully 3 per cent. of the total ore charged, which aggregates the large amount of approximately a million and a quarter tons per annum in this country. Until within a few years, this dust has been thrown away or used as filling, although containing about 40 per cent. metallic iron.

For many years efforts were made to use this material by compressing it into briquettes, but the cost of the operation, together with the fact that the briquettes disintegrated and the dust was again blown out, led to an abandonment of the briquetting plants.

The first commercially successful method of utilizing the dust was discovered by passing the material through the cement kilns at South Chicago. Experiments showed that with the proper heat treatment the coke dust could be burned off and the iron ore conglomerated into nodules or nuggets averaging over 60 per cent. iron content. These nodules, when fed to the blast furnace, were easily and completely reduced. The fact that the sinter of the flue dust contains such a high percentage of iron and that all of the sinter is reduced, together with its physical shape assisting the steady movement of the charge downward in the blast furnace, thereby preventing

so-called slips, makes the sinter more valuable per ton than any ore.

It was necessary to derive mechanical means for preventing the accumulation of the sinter on the walls of the kiln. Plants have been in operation for some years using this process, with endless chains carrying scrapers constantly passing forward through the kiln, and cooled in water on their return outside of the kiln.

Recently other methods of utilizing dust have been devised which may prove successful commercially, and the indications are that within a short time the greater portion of this former waste will be prevented.

The development of the Portland cement industry in this country and the extension of its uses have been marvelous, and the following table shows a remarkable increase in the production of Portland cement in the United States every year since 1895, when this country first reached the production of approximately one million barrels:

Year.	Production of Portland cement of United States Barrels.	Production of Universal Portland cement barrels	Percentage of Universal to total American production of Portland cement.
1895.....	990,324
1896.....	1,543,023
1897.....	2,677,775
1898.....	3,692,284
1899.....	5,652,266
1900.....	8,482,020	32,443	0.39
1901.....	12,711,225	164,316	1.29
1902.....	17,230,644	318,710	1.85
1903.....	22,342,973	462,930	2.08
1904.....	26,505,881	473,294	1.78
1905.....	35,264,812	1,735,343	4.92
1906.....	46,463,424	2,076,000	4.55
1907.....	48,785,390	2,129,000	4.36
1908.....	51,072,612	4,535,000	8.89
1909.....	62,508,461	5,786,000	9.27
1910.....	73,500,000—Gov. est.	7,001,500	9.52

It may be of interest to note the increasing percentage of the total American production shown by universal Portland cement, which is the only Portland cement manufactured in this country using slag as one of the raw materials. With the new plant now approaching completion the aggregate production of Universal Portland cement in the Chicago and Pittsburgh districts will amount to over one-eighth of the country's total. Expressed in weight, the output of the finished product will be over two million gross tons per annum. Our plants in the Chicago district will consume all the available slag that is suitable for the purpose from an aggregate of nineteen blast furnaces in the South Chicago works of the Illinois Steel Company and in the Gary Works of the Indiana Steel Company.

Comparing the pig iron production and Portland cement production of this country in figures of long tons, the percentage of Portland cement to pig iron in 1890 was six-tenths of 1 per cent., in 1900 $10\frac{3}{10}$ per cent., and in 1910 47 per cent. The continuation of any such relative growth would mean that before 1920 the tonnage of Portland cement would considerably exceed that of pig iron. I would hesitate, however, to predict that such would be the case.

Portland cement is defined by the United States Government as the product obtained from the heating or calcining up to incipient fusion of intimate mixtures, either natural or artificial, of argillaceous with calcareous substances, the calcined product to contain at least one and seven-tenths times as much of lime, by weight, as of the materials which give the lime its hydraulic properties, and to be finely pulverized after said calcination, and thereafter additions or substitutions for the purpose only of regulating certain properties of technical importance to be allowable to not exceeding 2 per cent. of the calcined product.

From this definition it will be seen that the raw material for Portland cement is not limited to any particular form of material, it may be made from any combination of materials that together furnish the proper elements. In this country Portland cement is manufactured from a number of raw materials, which, with a few exceptions, may be classed under four heads:

First.—Argillaceous limestone (cement rock) and pure limestone.

Second.—Clay and shale and limestone.

Third.—Clay or shale and marl.

Fourth.—Slag and limestone.

In all cases the raw mixture is a combination of some form of clay and some form of lime, and in the first and fourth classifications the clay materials contain some lime. This simply reduces the proportion of lime material necessary for a proper mixture.

In the manufacture of Portland cement from slag and limestone the molten slag flowing from the furnaces is granulated by a stream of water, loaded into cars and transported to the cement plants, where it is dried in rotary driers, and receives the first grinding; it is then mixed in automatic weighing machines, with the proper proportion of ground and dried calcite limestone. These are then ground together and burnt to a hard clinker at a temperature of nearly 3000° F. in rotary kilns, using pulverized coal for fuel.

This clinker, after seasoning, is crushed and ground and mixed with a small percentage of gypsum to regulate the setting time. The cement is ground to such fineness that 96 per cent. passes through a sieve having ten thousand meshes, and 80 per cent. passes a sieve with forty thousand meshes to the square inch. It is then conveyed to the stock house for storage prior to shipment.

It is necessary to use a flux in furnaces supplying slag for cement manufacture, a pure calcite limestone. The limestone burnt with the slag must also be a pure calcite stone. It is also essential that the ores be of a uniform and proper character.

Inasmuch as Lake Superior ores are noted for their remarkable uniformity of analysis, the resultant slag obtained from the use of these ores and a pure calcite limestone is more uniform in its analysis than any form of natural clay deposits used in the manufacture of Portland cement, and the variation in the proportions of the two raw materials used in the manu-

facture of Portland cement from slag is less than those of any other materials mentioned above.

In addition, the opportunity for analysis and selection of the proper ingredients through the use of an artificial material is a great advantage as compared to the necessitous use of natural materials just as they are found with their variations in analysis at different depths.

In the intense heat of the kiln, under the influence of the oxidizing flame, any sulphides in the slag are completely burned out.

The rotary kiln commonly used ten years ago was sixty feet long and six feet in diameter. This has gradually been increased in length and diameter until the modern kiln is one hundred and forty to one hundred and fifty feet long and eight to ten feet in diameter, and there are a few even larger kilns in use. Kilns are usually set at an incline of three-quarter of an inch to the foot. With the lining and content the modern kiln weighs one hundred and fifty tons and in revolving upon two bearings presents interesting constructional features.

In the case of the plant at Buffington, Indiana using twenty-six thousand horse power, situated between South Chicago and Gary, Indiana, electric power is supplied at twenty-two thousand volts from the steel works at these points. Each piece of machinery is driven by its individual motor, supplied with alternating current at four hundred and forty volts. The high tension line is connected through the cement plants, and the gas engines at these two steel works fourteen miles apart, operate continually in parallel. This enables the cement plant to draw its power from either source, or from both sources at the same time as may be desirable. It has happened that one of these works has supplied power to operate the cement plant and furnished additional power at the same time to the steel works at the other end of the line.

The method of manufacture above described is the standard method of manufacturing Portland cement from natural deposits, and the finished product differs in no way from other Portland cements in chemical analysis, fineness, specific gravity, color, nor in the operation in practical work. It has no peculiarities whatever and has no limitations as to its applications. There is no difference, from the chemical point of view, between the manufacture of Portland cement from natural deposits, such as limestone and clay or shale, and its manufacture from limestone and slag. Slag is really a mixture of the clay from the deposit with the lime content of the stone used as a flux in the furnace.

Our method of manufacture of Universal Portland cement does not embody any real invention, nor is it based on any patents. It is simply an adaptation to an artificial raw material of the regular Portland cement process formerly applied only to natural deposits.

True Portland cement in which slag is used as one of the raw materials should not be confused with puzzolan or so-called "slag cements" which are simply mechanical mixtures of slag and slaked lime.

ground together without burning. Such cements are suitable only for use under ground and in moist locations.

The manufacture of Puzzolan cements in this country has practically been abandoned.

The remarkable growth of the Portland cement industry is not equalled by any other manufactured article. This is due to the economy, durability, and plasticity of cement and concrete work. While large engineering work, such as dams, bridges, and heavy reinforced concrete buildings, consume large quantities of cement, the bulk of consumption at the present day is in a multitude of small uses. It takes an average shipment of only five barrels a day to take care of the average customer of a large cement company.

For example, there is a steady increase in the application of cement to new uses on the farm, such as silos, fence posts, barn floors, feeding floors, watering troughs, corn cribs, etc. There, as elsewhere, concrete is rapidly displacing all forms of wood construction, this process being hastened by the continually advancing cost of lumber.

Beautiful effects are now being obtained in concrete surface finishes and its use in decorative work is advancing rapidly.

The use of Portland cement will continue to increase until the campaign of education of the small user has reached its finality. In this direction a great work is being done to educate the general public in the proper use of cement by individual manufacturers by the Association of American Cement Manufacturers, and by the cement shows which are given in several of the largest cities every year.

In conclusion, it will be seen from the foregoing that most of the problems of utilization of wastes or by-products of the blast furnace have been solved, and that these solutions, in addition to being highly profitable, are powerful factors towards the conservation of our natural resources.

Portland cement manufactured from slag, to a large extent, replaces wood; the waste gases displace coal, and reclamation of the flue dust conserves the deposits of iron ore.

THE TECHNICS OF IRON AND STEEL.¹

By THEODORE W. ROBINSON, Vice-President, Illinois Steel Co., Chicago, Ill.

Received May 22, 1911.

The basis of modern civilization is the increased productiveness of labor and the accumulated wealth that has resulted from the universal use of iron and steel. The manufacture of iron and steel represents a comprehensive application of scientific research and discovery, and the indebtedness of society to our institutions of technical learning is exemplified in no more forceful way than by their influence upon our most important industry. Human progress since medieval times has been closely allied with iron's progress. The essential elements of existence have

ever been food, raiment, habitation and transportation, and the difference between our modern conditions and the conditions of the past is fundamentally the difference of the labor efficiency with which these necessities are produced. Closely analyze all the fields of human endeavor and, whether it be in the essentials of existence or the luxuries of life, somewhere the world's greatest metal will be found playing a vital part. The political demarcation of nations has been wrought and maintained by the war products of the foundry and the forge, but it is in the realm of industry that there has been found that potency of iron which has caused the progress of the last century to surpass the accomplishments of twenty centuries. Let him who questions this statement compare the average conditions of living within these periods, and let him recall that the revolutionary inventions of modern civilization are directly due to or have been permitted by the use of our most precious metal.

It is manifestly impossible in a brief address to trace the evolution of the iron and steel industry, much less to attempt a detailed description of its manufacture. We may, however, briefly discuss some of the salient changes and economies that have taken place within the past fifty years. The underlying principles of the manufacture of iron and steel are the same to-day as they were half a century ago. The mining of ore, of coal, and of limestone; the manufacture of coke; the smelting of these raw materials into pig iron; the refining of pig iron into wrought iron or steel, and its rolling or forging into the finished product—all these steps are essentially the same as they were before; and the blast furnace, converter, open-hearth furnace and rolling mill are still the agents of reduction and conversion. No industry has been more ready to recognize the merits of discovery and invention, or quicker to reap the benefits, and a well equipped iron and steel plant is to-day the very embodiment of applied science. To this is due the fact that as measured by quality, quantity, cost, and diversity of product, the efficiency of former operations has been revolutionized.

It is of interest to briefly record the progress made in this country in the manufacture of iron prior to 1860, partially that we may have a better conception of the remarkable development that has followed. The first pig iron made in America was manufactured in 1644 at Lynn, about ten miles from Boston, and there, too, was refined the first bar iron made in this country. The capitalization of this pioneer enterprise was \$5,000, and a skilled workman commanded a wage of about 55 cents a day. Referring to this industry, Governor Winthrop said that, "the iron work goes on with more hope, it yields now about seven tons per week." Such was the inception of the American iron and steel industry, and with the little plant at Lynn as a nucleus, Massachusetts for a hundred years after the settlement at Plymouth was the chief seat of this country's activity. To the Boston iron works the credit is due of rolling in 1846 some of the first iron T rails ever produced in America, and fifty years ago Massachusetts was still one of the most

¹ Presented before the Congress of Technology at the Fiftieth Anniversary of the granting of the charter of the Massachusetts Institute of Technology.

important centers of our nail industry. Even at this later period our iron plants consisted of small units of mine and mill located throughout the country with special reference to the proximity of local ores, fuel and water power facilities.

But the industry was expanding, and the year before the Massachusetts Institute of Technology was founded America produced a little over 900,000 tons of pig iron. An index of the accomplishment of fifty years prior and subsequent to 1860 is had in the 1810 production of 54,000 tons of pig iron, as against over 27,000,000 tons of pig iron produced in 1910. Such a phenomenal growth has, of course, been made possible by our wealth of natural resource; but raw material is of but potential value until won by the arts of industry, and even when converted is largely valueless until transported to its point of consumption. Cheap conveyance is a vital factor and the beneficent influence of iron and steel upon the progress of prosperity of this nation and of the world finds no more striking exemplification than its use in the art of transportation. Without the steel rail our prairies, forest and mines would still largely lie in their pristine glory and the interior fastnesses of the continents would be inviolate. Fifty years ago this country had but 30,000 miles of railroad. Transportation was expensive, slow and served little more than the important centers. The Pacific Coast was many weeks distant from the Atlantic Seaboard and the stage-coach and the pony express were essential elements of communication. The maximum capacity of the freight cars on the Pennsylvania Railroad was 9 tons, and our waterways largely dominated our commerce and industry. To-day our country is served by 240,000 miles of railroad; our freight cars are of fifty and even 100 tons capacity and the cost of transportation has been so lowered that the average remuneration of at least one of our large systems is less than five mills per ton mile. The effect of these changes is partially indicated by the 23,000,000 immigrants who have come to this country since 1860, by the increase of 60,000,000 in our inhabitants, and by the rapid movement westward of the center of our population.

But how comes it that in the short span of less than a generation such strides could be made in an industry which has basically changed but little? The application of scientific research is alone responsible and it is primarily responsible because it made possible the economic development of the Bessemer and open-hearth processes, which were given to the world a few years prior to 1860. The Bessemer process was a metallurgical failure until Mushet's discovery of the efficacy of carbon and manganese addition, and it could not have been a commercial success without the mechanical improvements of many later workers in the field. The success of the open hearth was even slower. The development of the steel industry accentuated the necessity of exact methods. The comparatively rough-and-ready way of producing wrought iron would not answer for the more difficult accomplishment of high-grade steel. As it became

recognized that the price of success was the scientific vigilance of technical men, the chemist, the metallurgist, the mechanical engineer, the steam engineer and the electrical engineer—all became essential factors. In the early stages, tonnage, as an essential element of cost, was a main consideration. Now quality stands first, and while tonnage has gone apace, the strict inspection that commands product to-day subordinates volume to character. Under our superlative wealth of natural resource and under our insistent demand for maximum output, the questions of waste and conservation were secondary questions and the time and money involved in the utilization of by-products were not thought commensurate with the return. But scientific management has brought about a new order of things: the selection and use of the raw materials entering into the manufacture are all subject to the analysis and control of the chemical laboratory. Chemistry is the monitor of the various steps in the transformation of ore to the finished product and with the physical laboratory stands sponsor for both the twelve-inch gun and the almost invisible wire that is drawn through the diamond die. Nearly every domain of science is called upon. The knowledge and control of heat is fundamental in the development of power and in the reduction of fabrication of steel. The essence of economic production lies in an intelligent application of the laws of hydraulics, hydrostatics, thermodynamics, and strength of materials. Electricity and magnetism play a prominent part in the transmission of power and illumination, and the refining of steel by electric energy is a departure destined to have an important future.

A modern steel plant is indeed a complex and wonderfully efficient machine. The remarkable influence that steel has exerted in the last century has been made possible by the radical reduction in its cost of manufacture. The price of steel rails affords a measure of what has been accomplished in this regard. Less than fifty years ago steel rails made their advent in this country at an equivalent of approximately 8 cents per pound. To-day rails sell for 1 1/4 cents per pound, or less than one-sixth of their former cost. While the reduction in cost during the last decade is naturally proportionately less than in the few decades that preceded, it is significant that in spite of the general increase in the prices of commodities the relative price of steel in this country, as shown by the commodity index, has continued to decrease in recent years. It is an eloquent testimony to the efficiency of modern methods and to the conservatism of our iron masters that this has been accomplished in spite of the decreasing richness of our ores and a substantial increase in the cost of both labor and material.

In studying the causes of our cost reductions, two prominent factors appear. First, the fuel required to convert ore into a finished product has been largely reduced; second, the intensity of production, which roughly measures the increased efficiency of labor, has been enormously increased. At the mine, in transportation, at the furnace and in the mill, na-

chinery has taken the place of men, and a man in the steel industry to-day accomplishes from ten to fifty times as much work as did his predecessor fifty years ago.

In 1860 a thousand tons of pig iron per month was an extraordinary production for a blast furnace, and one and a half gross tons of coke was required for each gross ton of pig iron produced. To-day an output of 18,000 tons per month from a single furnace excites little comment, and the average coke consumption of the modern American furnace is a gross ton of coke for each ton of pig iron. This increase in tonnage, and decrease in fuel is the result of the uniformity and enlargement that has followed scientific management and not because of any radical departure in blast-furnace practice. In the refining of pig iron the gas producer, the regenerative furnace, the hot metal mixer, and the improvement in our prime movers have been important elements in the reduction of fuel; but it is mainly due to the substitution of the open hearth and the Bessemer converter for the puddle furnace that we are able to produce steel with nearly one-fourth less coal than was formerly required to produce iron. Our prime movers fifty years ago consisted essentially of slide valve steam engines in conjunction with low-pressure flue boilers, having an over-all efficiency of but 4-5 per cent. of the total heat in the fuel realized as work in the engine. To-day high-pressure water tube boilers and compound condensing engines with efficient valve gear have more than doubled the thermal efficiency, and the combination low-pressure steam turbine and non-condensing compound steam engine gives us a thermal efficiency of even 16 per cent. In other words, one ton of fuel with such an installation is able to do as much work as four tons of coal was formerly able to do.

The introduction of the gas engine marks another epoch in power production. With a thermal efficiency of 25 per cent., a given quantity of blast-furnace gas produces in the gas engine at least twice the amount of power obtainable with the modern boiler and steam engine. The gas engine when combined with the electric generator permits the highest development in plant concentration and in the production and transmission of power. With modern equipment the blast furnace produces a surplus amount of gas over and above its own heat and power requirements equivalent to at least 500 pounds of coal for each ten of iron produced. A notable example of the efficient use of blast-furnace gas as a by-product is presented in the new Gary, Indiana, plant of the United States Steel Corporation. There has been erected or is in process of installation over 100,000 horse power in gas engine units varying from 2,500 horse power to 4,000 horse power each, and the contemplated plant when finished will have more than 200,000 horse power in gas engines using blast-furnace gas. These, when aided by the surplus gas from the connected by-product coke ovens, will not only furnish all the heat, light and power required for all the mill departments, practically without the aid of coal, but will afford,

as well, a substantial surplus available for neighboring industries.

It can be readily appreciated, therefore, that the aggregate saving of fuel in the iron and steel industry must be enormous, and one whose effect upon the conservation of the nation's coal supply must be important. The following figures based upon actual practice give an approximation of what this annual saving amounts to. Last year the United States produced 27,298,545 tons of pig iron and 25,917,281 tons of Bessemer and open-hearth steel. Had the same coke ratio been required to smelt this pig iron as that required in 1860 we should have used 23,000,000 net tons of coal more than we actually did use. Moreover, had the pig iron which was converted into steel last year been converted into wrought iron, we should have consumed 33,000,000 tons more coal than that which was actually burned. The measure, then, of last year's fuel economy in our iron and steel industry was approximately 56,000,000 tons of coal. But this is not all. The production of coke in the United States last year was about 41,000,000 net tons, made mostly in the bee-hive oven. Had this same tonnage of coke been produced in by-product coke ovens, 10,000,000 tons less coal would have been required and there would have been an additional saving of by-products in surplus, gas, tar and ammonia of a value of \$39,000,000. Basing our calculations on 1910 production and giving coal an arbitrary value of a dollar a ton, these savings in the iron and steel and coke industries amount to \$107,000,000 per year, as the sum of what we have done and what we will shortly do toward the conservation of our coal supply.

Such are some of the savings that have permitted our manufactured products to successfully enter the markets of the world. The United States has been one of the world's great granaries. The United States is now one of the world's great workshops. Fifty years ago our exported foodstuffs surpassed in value the exports of all our manufactured products. To-day the value of our manufactured products sold abroad largely exceeds the value of the shipments from our farms. In 1860 we exported iron and steel to the value of \$6,000,000. Last year we contributed \$179,000,000 in iron and steel to the markets of the world.

While we are largely indebted to the development of the natural sciences for such results, the technics of iron and steel embrace a wider field. The science of modern organization and the ethics of management represent in themselves as marked a departure as we find in the actual operations of our works.

Half a century ago the ownership and control of our iron works lay largely in the individual, by actual ownership or through small organizations. Plants were small and comparatively numerous. There was close contact between employer and employee and the workmen were few and their duties correspondingly varied. The economies of specialization, intensity and concentration were largely unknown or impractical.

To-day our mines and mills are principally con-

trolled by large corporations. Ownership stands in thousands of small and widely scattered stockholders, and policy and operation are guided by their representatives. Plants are large and intensified production is commanded by armies of skilled men working with specialized machinery.

In achieving high efficiency and resultant low costs, the large corporation is an economic necessity. Its effectiveness in the elimination of waste is the power of large financial resource and concentrated direction. There is no better exemplification of the composite force of many owners than the plant at Gary. This, our latest extensive plant, has arisen in four years from the unbroken sand dunes of lower Lake Michigan, and is a striking illustration of the possibility of \$55,000,000 when expended by a highly developed organization.

But the change that has come with our modern system is more than in the material improvement of plant and machinery. There has followed a clearer conception of the relationship of the public, the wage earner and the investor. Industrial success means

loyalty and team work, and intelligent management appreciates that profits if they are to be sustained must not be preferential to justice and humane treatment. Coöperation with one's competitors, pension funds for the superannuated, systematic endeavor for the prevention of accidents, voluntary compensation for the injured, recognition of faithful service, elimination of Sunday work, profit-sharing, sanitary surroundings, the club, the hospital—all these are manifestations of a humane and efficient policy.

Business administration in our complex industrial life embodies many elements beside the natural sciences. There is the science of men as well as the science of machines, and both are necessary for the broadest type of industrial efficiency.

A training that is either too cultural or too specialized does not harmonize with present requirements and the Massachusetts Institute of Technology, in recognizing the commercial as well as the technical needs of the times, is but maintaining her tradition for progressive thought and leadership in method.

SCIENTIFIC SOCIETIES.

INDIANAPOLIS MEETING, AMERICAN CHEMICAL SOCIETY.

Four hundred and thirty-two members and guests attended the summer meeting at Indianapolis, which was the largest summer meeting of the American Chemical Society ever held. The meeting was an unusually successful one, both from the standpoint of work accomplished and the general enjoyment of those present.

Those members who appeared a day early were treated to an automobile ride around the famous Indianapolis Speedway, followed by a dinner at the University Club.

The general meeting itself opened on Wednesday morning, June 28th, with an address by Charles Baskerville, on "The Chemistry of Anesthetics," and by W. Lash Miller, on "The Chemical Philosophy of High School Textbooks." At the close of this session Dr. W. F. Hillebrand presented a preliminary report for the Committee on the Quality of Platinum Laboratory Utensils, which was afterwards discussed in the sessions of the Industrial Division.

The hospitality of the local members knew no bounds and a complimentary luncheon was served each day. Also an unusually attractive complimentary "smoker" was held at the German Club House on Wednesday night, at which mementoes were distributed, consisting of bakelite cigar holders, watch fobs bearing the Society's emblem, and steins, also stamped with the Society's pin in blue and gold. On Thursday evening a public lecture by A. D. Little on "The Earning Power of Chemistry" was delivered at the German House, followed by a concert in the German House gardens. Visits to manufacturing plants were a feature of the meeting, among which should be especially mentioned Eli Lilly & Co., the Van Camp Packing Co., Kingan & Co., E. C. Atkins & Co., Encaustic Tile Co., Nordyke & Marmon Automobile Co.,

Fairmount Glass Works, the Indianapolis Water Works, and the Polk Sanitary Milk Co. An especially interesting program was also arranged for the visiting ladies, all of whom expressed themselves as thoroughly pleased with the entertainment given.

On Friday evening nearly two hundred members and guests gathered at the Columbia Club for the usual midsummer banquet. The banquet was a great success. The tables were decorated with flags and flowers, the menu offered was of the best and the speeches were greatly enjoyed. Dr. H. W. Wiley acted as toastmaster and introduced as the special speakers of the evening Governor Marshall, of Indiana, and ex-Vice-President Fairbanks. Many ladies attended the banquet, which was also graced by the presence of Mrs. Marshall. One of the best orchestras in the West furnished music during the evening.

A transcript of the minutes of the meetings of the Industrial, Fertilizer, Agricultural and Food, and Pharmaceutical Divisions follows, as well as an account of the meeting of the Rubber Section. The record of papers in the Organic, Physical and Inorganic Divisions and the Biological Section will appear in the regular proceedings of the Society.

Division of Industrial Chemists and Chemical Engineers.

GEORGE D. ROSENGARTEN, *Chairman*.

Dr. Rosengarten thanked the Division for his election and requested the earnest coöperation of its members in order to secure papers of value and further the work of the Division.

The reading of the minutes was dispensed with.

The report of the secretary was read and accepted, of which the following is an extract:

"The secretary has to report for the Executive Committee that since the last meeting they have elected as Chairman of the Division in the place of George C.

Stone, resigned, George D. Rosengarten, of Philadelphia. They have also approved of the proposal made by the Committee on Methods of Analysis of Glycerine, which is a sub-committee of the Industrial Division Committee on Analysis of Soap and Soap Products, that they coöperate with the International Committee on Glycerine Analysis and unite with the International Committee in the preparation of a joint report if it appears to the said committee advisable to do so.

"There has been a slight increase in the membership of the Division since the last meeting, the number of registered members now being about 1,050."

The secretary further presented a financial statement and reported on the present status of the technical directory, which can be published as soon as sufficient funds are available.

The Report of the Committee on Soap Products and Glycerine, read by Professor Langmuir, was discussed and accepted.

The Report of the Committee on Official Specifications was read in part, and the committee continued.

No report was made by the following committees:

Definition of Trade Terms,
Research Problems,
Standard Methods of Analysis,
Descriptive Bibliographies,
Publicity,
Special Compounds.

The Report presented by Dr. Hillebrand on the "Quality of Platinum Laboratory Utensils" was discussed by Professor Langmuir, William Brady, F. C. Phillips, and John White.

The Report of the committee appointed to draft resolutions regarding the retiring Chairman, Arthur D. Little, was made, and it was

VOTED: To adopt these resolutions and to spread them on the minutes to become a part of the permanent records of the Division.

The following papers were read:

"Hop Standards: Considered from the Chemical Standpoint," by H. V. Tartar, showing the different results obtained by the different methods of analysis, compared with results from the author's own methods.

"Losses in the Storage of Coal," by Horace C. Porter and F. K. Ovitz, showing that under usual conditions and not piling too high, coal is not changed in storing, wet or dry.

"Refractories and Laboratory Appliances made from Alundum," by P. A. Boeck. Exhibition of samples and statement as to its usefulness, discussion by White and Hillebrand.

"Determination of Vanadium in Vanadium and Chrome-Vanadium Steels," by John R. Cain; read by Dr. Hillebrand.

"Need of Professional Code of Ethics among Chemists," read by Lucius P. Brown, substitute for Francis L. Parker; discussed by Charles C. Kawin, A. D. Little, Edward A. Barrier, Bronzius, H. V. Farr, in favor of certification, public and technical. McCormack favored such plan.

On motion of Mr. Bryan, seconded by Mr. Handy, it was

VOTED: That the chairman of the Division appoint a committee to consider the question of the need of a professional code of ethics among chemists.

On motion of James O. Handy it was

VOTED: That the Division of Industrial Chemists and Chemical Engineers recommend to the attention of the Directors of the American Chemical Society the advance publication and circulation of certain papers, in order to bring out discussion.

That we further suggest the desirability of having the discussions at our meetings reported accurately.

"The Examination of Fir Oil Obtained by Steam Distillation of Douglas Fir," by Henry K. Benson and Marc Darrin; read by Horace G. Byers.

"The Wood Distillation Industry of the Pacific Northwest," by Henry K. Benson; read by Horace G. Byers.

"Ratfish Oil as a Paint Material," by Henry K. Benson and Wallace Eshleman; read by Horace G. Byers.

"Analysis of Commercial Nitrous Oxide," by W. R. Smith and E. D. Leman; read by secretary.

"A Differential Test for Sulfur-chloride and Sulfur-dioxide Substitutes," by Charles P. Fox; read by secretary.

"Marine Fiber," by Charles P. Fox; read by chairman.

"A Method of Analysis of Lead Ores," by John Waddell; read by secretary.

"A Method of Analyzing Some Commercial Gold Alloys," by James O. Handy.

"Concentration and Purification of Iron Ore, High in Sulfur, by Roasting in a Rotary Kiln," by James O. Handy. Temperature and speed in the desulfurization of iron ores seemed to be the theme of the paper, which called forth quite a little discussion on methods and apparatus.

The following papers were read by title:

"The Rapid Analysis of Alloys," by Guillermo Patterson, Jr.

"The Testing of Inks, Typewriter Ribbons and Carbon Papers," by Percy H. Walker.

"Storage Battery Efficiency," by J. S. Staudt.

"A New Modification of Gas Analysis Apparatus," by B. G. Klugh.

"Determination of Dust in Blast-Furnace Gas," by L. A. Touzalin.

Dr. Rosengarten adjourned meeting.

GEO. P. ADAMSON,

Acting Secretary.

Division of Fertilizer Chemistry.

The meeting of the Fertilizer Division was called to order by the chairman, Mr. P. Rudnick.

The minutes of the last meeting were read and approved.

The following was the program:

"Note on the Permanganate Methods for Availability of Organic Nitrogen," by John Phillips Street.

"The Use of Fused Silica Dishes for Potash Determination in Fertilizers," by W. D. Richardson.

"The Availability of the Insoluble Nitrogen in Certain Commercial Fertilizers," by B. L. Hartwell and F. R. Pember.

"The Use of Alundum Crucibles for Total Phosphoric Acid and Potash Determinations in Fertilizers," by W. D. Richardson.

"The Availability of Nitrogen in Complete Fertilizers," by Jacob G. Lipman.

"Notes on Estimation and Valuation of Potash," by P. F. Trowbridge.

Report of committees:

Paul Rudnick, for the Committee on Nitrogen.

G. A. Farnham, for the Committee on Phosphoric Acid.

J. E. Breckenridge, for the Committee on Potash.

C. F. Hagedorn, for the Committee on Phosphate Rock.

F. B. Carpenter, for the Committee on Fertilizer Legislation.

On motion regularly made and seconded it was decided that the publishing of the Nitrogen Committee Report in full be referred by the Executive Committee to the Council, and then, if favorably received, members of the Fertilizer Division be asked for contributions to cover cost of publishing.

On motion meeting adjourned.

J. E. BRECKENRIDGE,
Secretary.

The Division of Agricultural and Food Chemistry.

The meeting was called to order by the chairman, Mr. H. E. Barnard.

The following papers were read:

"Composition of the Drainage Water of a Soil with and without Vegetation," by T. L. Lyon and J. A. Bizzell.

"The Cryabiatic Point," by W. D. Richardson.

"The Analysis of Canned Tomatoes," by E. H. S. Bailey and H. L. Jackson.

"The Chemical Changes which Take Place during the Spoilage of Tomatoes, with Methods for Detecting this Spoilage in Tomato Products," by R. F. Bacon and P. B. Dunbar.

"The Action of Non-Acid Foods on Tin Containers with Special Reference to Canned Shrimp," by R. F. Bacon and W. D. Bigelow.

"Determination of Tin in Food Products," by Edward Gudeman.

"A Chemical Study of Certain 'Sand-Hill' Soils of South Carolina," by T. E. Keitt.

"A Short Method for the Determination of Soluble Arsenic in Commercial Lead Arsenates," by T. O. Smith and B. E. Curry.

"Methods of Estimating Fat in Tissues," by Walde-
mar Koch.

"The Effect of Phosphorus Manuring on the Amount of Inorganic Phosphorus in Slat Turnip Roots," by Burt L. Hartwell and Frederick S. Sammet.

"The Detection and Determination of Small Quantities of Ethyl Alcohol, Methyl Alcohol and Formic Acid," by R. F. Bacon.

"The Determination of Malic Acid," by P. B. Dunbar and R. F. Bacon.

"Detection of Benzoic Acid in Coffee Extract," by H. C. Lythgoe and C. E. Marsh.

"Composition of Tincture of Ginger Made with Varying Strengths of Alcohol," by H. C. Lythgoe and L. I. Nurenberg.

"Akron (Ohio) Water: Home Treatment for Bath and Laundry," by Charles P. Fox.

The following papers were read by title:

"Two New Pieces of Apparatus. (a) Apparatus for the Continuous Extraction of Liquids with Immiscible Solvents Lighter than Water. (b) A Complete Apparatus for Quantitative Determinations Based on the Measurement of an Evolved Gas," by R. F. Bacon and P. B. Dunbar.

"The Influence of the Reaction of Solution on the Development of Wheat Seedlings," by J. F. Breazale and J. A. LeClerc.

"The Distribution of Organic Constituents in Soils," by Oswald Schreiner and Elbert C. Lathrop.

"Dihydroxystearic Acid in Good and Poor Soils," by Oswald Schreiner and Elbert C. Lathrop.

"Studies on Organic Soil Nitrogen," by Elbert C. Lathrop and Bailey E. Brown.

"The Composition of the Timothy Plant at Different Stages of Growth," by L. D. Haigh and P. F. Trowbridge.

"The Volatile Acids of Corn Silage," by Arthur W. Dox and R. E. Neidig.

"The Arsenic Content of Shellac and the Arsenical Contamination of Food Products from that Source," by H. B. Smith.

"The Solubility of Lime in Contact with Clay and Water," by B. E. Curry.

The Division considered the advisability of adopting by-laws to govern its meetings and referred the matter to the Executive Committee with power to draw up a set of by-laws and present them at the next meeting for action.

It was pointed out that the expenses incidental to the meeting such as typewriting and postage had heretofore been borne by the President and Secretary of the Section and the Division voted that the bills incurred in this manner regarding the present meeting be referred to the Finance Committee with the recommendation that they be paid from the treasury of the American Chemical Society.

It was also voted that the Council be requested to assign to the Division of Agricultural and Food Chemistry papers on Sanitary Water Analysis and Supplies.

Respectfully,

W. D. BIGELOW,
Secretary pro tem.

Division of Pharmaceutical Chemistry.

The first session was called to order by the chairman, Mr. B. L. Murray, eighteen members being present.

The chairman stated that he had no address to read, but spoke of the progress which the Division had made, commenting especially upon the increase in membership from 66 at the beginning of the year to 150 at the present time.

The secretary presented a report telling of the work

done to increase the membership and, as treasurer, reported collections amounting to \$66.50, expenses amounting to \$39.00 and a balance of \$27.50.

Methods of promoting the growth and activity of the Division were then discussed and it was agreed that the work of the Committee on Quantitative Methods offered the best means of interesting the members in the work of the Division; and that the work of this committee should be extended. No action, however, was taken at this session.

The following motion by A. D. Thorburn was adopted:

That the Division expresses its approval of the secretary's action in trying to secure new members, and of the expenses thus incurred, and directs that the campaign for members be continued as far as the time of the secretary and the funds available will allow.

The following papers were read by the secretary and were discussed by several members:

"The Determination of Camphor in Spirits of Camphor," by L. D. Havenhill.

"Rapid Determination of Beeswax and Honey," by Fred Klein.

The following papers were read by title:

"The Volatile Acidity of Tragacanth and Other Gums," by W. O. Emery.

"Acetate Collodion," by E. C. Worden.

C. H. Briggs then read a paper on "The Estimation of Minute Quantities of Nitroglycerin," by W. L. Scoville.

After a brief discussion the meeting adjourned.

SECOND SESSION.

After the reading of the minutes of the previous session, W. A. Pearson gave an illustrated lecture on "The Manufacture and Testing of Drugs."

C. E. Caspari then read a paper on "Pharmacopoeial Revision," by Joseph P. Remington.

The reading of this paper was followed by an extended general discussion of pharmacopoeial matters.

THIRD SESSION.

The reading of the minutes of the previous session was dispensed with and after a brief report by the secretary, for the benefit of those not present at the first session, the Report of the Committee on Quantitative Methods was presented by F. O. Taylor, the chairman of the committee.

On motion by C. T. P. Fennel the report was received and on motion of C. E. Caspari a copy of the report was ordered to be sent to the chairman of the Pharmacopoeial Revision Committee.

Mortimer Bye presented the following motion:

That the present Committee on Quantitative Methods be retained; but that the number of members be increased at the discretion of the chairman of the Division, and that the scope of the work be enlarged by the committee.

This motion was duly seconded and after discussion by Messrs. Caspari, Rosengarten, Taylor, Fennel, Eldred, and Murray was carried.

L. A. Brown then presented his paper on "Aromatic Spirits of Ammonia."

The following papers by Edw. Kremers were read by title:

"Precipitated Sulphur, a Study of a Dermatological Prescription."

"The Moisture Content of Drugs."

C. M. Pence then presented his paper on "A Study of the Bromine and Iodometric Methods for the Determination of Resorcinol."

C. E. Caspari suggested that a copy of this paper be sent to the chairman of the Pharmacopoeial Revision Committee.

A. D. Thorburn presented a paper on the "Estimation of Morphine by Extraction with Phenyl-Ethyl Alcohol."

The following papers were read by title:

"The Relation of the Alkaloids of Gelsemium to One Another," by L. E. Sayre.

"Notes on the Iodometric Determination of Strength of Formaldehyde Solutions," by J. S. Chamberlain.

"The Pharmacopoeial Standard for Desiccated Thyroid Glands," by Reid Hunt and Atherton Seidell.

E. G. Eberhardt presented two papers on "A Modified Form of Repercolation" and "Tincture of Cantharides."

H. T. Graber read a paper on "Some Observations upon the Assay of Digestive Ferments."

C. H. Briggs presented a paper by C. F. Ramsay on "A New and Accurate Method for Determining the Tryptic Value of Pancreatin," also a paper by A. Zimmerman on "The Accelerating Action of Hydrochloric Acid upon the Starch Converting Properties of Pancreatin and Malt."

H. T. Graber presented another paper by Mr. Zimmerman on "Laboratory Studies of Pepsin, Pancreatin, and Combinations of These Ferments."

The secretary read two papers:

"A Few Results Obtained from Pepsin Assay," by O. P. Eyre, and "Investigations made with Dry Egg Albumin in View of Replacing the Albumin Coagulated in the Egg, for Greater Accuracy in the U. S. Pharmacopoeia Pepsin Assay," by A. Zimmerman.

All of the papers on digestive enzymes were discussed collectively and it was suggested by A. H. Clark that, as a number of new facts had been brought out, copies of these papers should be sent to the Pharmacopoeial Revision Committee. The meeting then adjourned.

FRANK R. ELDRED, Secretary

Meeting of the Rubber Section.

A preliminary meeting of the Rubber Section was held at 10 o'clock on June 30th at the German House, where a general consultation was held on the question of the continuance of the Rubber Section and also regarding means of increasing the activities of the members. The meeting was adjourned to 4 P.M.

The adjourned meeting was called to order at 4 P.M. at the Claypool Hotel by the secretary in the absence of the chairman with sixteen members present.

Dr. George Oenslager was elected temporary chairman and the minutes of the previous meeting, held in Boston, December 30, 1909, were read and approved.

Prof. Charles Knight submitted a report on prog-

ress from the Committee on Methods of Analysis. The report was accepted and the secretary directed to send mimeographed copies to all members of the Section.

The Committee on Specifications rendered a written report and the committee was discharged with thanks.

It was voted that the Section recommend to the Council of the Society that it appoint a Committee on Specifications, of the Rubber Section, to act in conjunction with a similar committee from the Division of Industrial Chemists.

It was voted that the Committee on Abstracts be discontinued.

It was voted that all members of the Section be asked to furnish the Committee on Methods of Analysis with their methods for the determination of acetone extract, free sulfur, total sulfur and ash in rubber; also that samples of rubber when sent out be sent to all the members of the Section who expressed a willingness to make coöperative analyses for purposes of comparison.

The meeting then adjourned.

FREDERICK J. MAYWALD, *Secretary*.

INTERNATIONAL ASSOCIATION OF CHEMICAL SOCIETIES.

On April 25, 1911, there was called together in Paris a preliminary meeting of delegates of the Chemical Society of London, the German Chemical Society and the Chemical Society of France, for the purpose of organizing an international association. The Chemical Society of London was represented by Messrs. Frankland, Meldola and Ramsay; the German Chemical Society was represented by Messrs. Jacobson, Ostwald, and Wichelhaus; the Chemical Society of France, by Messrs. Béhal, Haller and Hanriot. As a result of their deliberations the following by-laws for an international association were adopted.

ARTICLE I. An International Association of Chemical Societies is hereby founded.

ARTICLE II. The object of the Association is to form a bond between the chemical societies of the world in order to consider chemical problems of general and international interest.

ARTICLE III. All chemical societies can take part in the Association.

ARTICLE IV. The Association is directed by a Council formed from a certain number of members. Each country can be represented in the Council only by a single chemical society, which shall designate three representatives.

ARTICLE V. The existing Council consists of the delegates of the charter societies; namely, the German Chemical Society (*Deutsche Chemische Gesellschaft*), the English Chemical Society (*Chemical Society of London*) and the French Chemical Society (*Société chimique de France*). Representation of any society in the Council will be decided by the Council itself and by a majority of two-thirds of the members voting. Correspondence vote will be permitted in this case.

ARTICLE VI. The Council will fix at each reunion the time and place of the next session.

ARTICLE VII. The Council names at the beginning of each session a President, who is at the same time President of the Association and who presides at all functions until the end of the session.

ARTICLE VIII. The Bureau consists of the President, the Vice-President and the Secretary General, comprising the delegates from the same country.

ARTICLE IX. The President is charged to convene the Bureau; he will carry out the decisions of the Council, fix the order of the day for meetings of the Council, and formulate the relations between the different societies. The President will have approved the minutes of the meetings. However, the minutes of the last meeting can be approved by correspondence.

ARTICLE X. The work of the Association will consist of nomination of commissions in charge of studying questions submitted to them by the Council, publication in the journal of the affiliated societies or by any other method of publication which the Council may determine; conferences or congresses.

ARTICLE XI. The general expenses will be borne by the affiliated societies in proportion to the number of their members. All expenses other than general expenses will be charged to the different societies only under the individual agreement of the particular society. The Secretary-General shall submit at each session for the approval of the Council a financial statement for the interim.

ARTICLE XII. Modification of the present by-laws can be brought about only by a majority of two-thirds of the members of the Council. Correspondence vote is also permitted in this case.

During the session it was voted to invite the American Chemical Society, the Chemical and Physical Society of Russia, and the Union of Italian Chemical Societies to be represented in the Council and to name each three delegates. This invitation was only presented to the Council of the American Chemical Society at their Indianapolis meeting and after careful consideration, on motion of Past President John H. Long, the following vote was passed.

The American Chemical Society views with favor the proposal to join with the chemical societies of London, France and Germany in the formation of an international association on the lines suggested in the provisional program forwarded by Professor Ostwald, and the President of the American Chemical Society is hereby empowered to enter into correspondence on the details of the proposed organization.

CHICAGO MEETING OF AMERICAN INSTITUTE OF CHEMICAL ENGINEERS, JUNE 21-24.

The third semi-annual meeting of the American Institute of Chemical Engineers was an important and successful event in the history of that society.

The chemical engineers were welcomed to Chicago by Mr. Wade, who represented the Mayor of Chicago, and by Dr. T. B. Wagner, representing the local committee.

Among the interesting papers presented was a very able address by the President, Dr. F. W. Frerichs.

"Methods of Attacking Chemical Industrial Problems," which was accompanied by complete detailed drawings and models of an installation for the manufacture of soda by the Solvay Process Company; also the great difference in both conditions and prices between this country and Germany was demonstrated by estimates on a process, which though successful in Germany, would prove a failure in the United States.

The report of the Committee on Chemical Engineering Education was read by Dr. Samuel P. Sadtler, chairman of that committee, and a paper discussing the "Four-Year Course in Chemical Engineering" was read by Professor J. H. James, of the Carnegie Technical School of Pittsburgh. A paper giving a summary of the work of the "Committee on Five-Year Engineering Courses of the University of Ohio" was presented by Professor J. R. Withrow.

Other papers presented were: "Industrial Chemical Calculations," by Professor J. W. Richards; "Rapid Determination of Tin in Food Products," by Dr. Edward Gudeman; "Distillation on the Continuous System," by Dr. C. L. Campbell; "The Institute and the United States Patent System," by Dr. William Grosvenor; "Practical Value of Calorific Tests on Anthracite Coal," followed by another on "Two Methods of Testing Asphalt," by Dr. S. F. Peckham.

A number of industrial excursions were made to plants among which was a visit to the plant of Messrs. Swift & Company.

The Toronto meeting of the American Electrochemical Society will be held September 21-23, 1911. There will be many interesting papers presented at this meeting.

EDUCATIONAL

The University of Maine recently conferred its Doctorate of Science upon Prof. Charles L. Parsons, of New Hampshire College, Secretary of the American Chemical Society.

Dr. K. Polstorff, Associate Professor of Pharmacological Chemistry at the University of Goettingen, Germany, died on June 20th at the age of 66 years.

Dr. P. Walden, Professor of Chemistry at the

Polytechnic School of Riga, Russia, has been elected a member of the St. Petersburg Academy of Sciences.

On June 26th Dr. Julian W. Baird, Professor of Chemistry and Dean of the Massachusetts College of Pharmacy, died at the age of 53 years.

Dr. Wm. C. Rose has been appointed Assistant Instructor in Physiological Chemistry at the University of Pennsylvania.

NOTES AND CORRESPONDENCE.

To the Editor of the "Journal of Industrial and Engineering Chemistry."

SIR:

In the July issue of your Journal, there is a communication from Dr. Leo H. Baekeland in which he discusses my Belgian patent relating to new condensation products, a brief notice of which appeared in your June number of this year. In reply to the same, I desire to explain that I have been too busy in commercially exploiting and developing these products and on other technical researches and enterprises to find time to produce any matter for publication other than patent applications, of which I have about forty now pending in the United States relating to this subject.

By invitation from the editor of THIS JOURNAL, I had previously promised to write an article on this subject, which will, I hope, follow this communication in the near future, as soon as the condition of pending applications for patents and my other work connected with the commercial development and exploitation of my inventions will permit.

It goes without saying and as a matter of course that if my Belgian patent gives my invention no approved standing as to novelty of subject matter and the proper restriction of my claims, neither do the Belgian nor French bakelite patents confer any such approved standing on bakelite.

But it should be clearly understood that from the beginning of my work, and at all times during and since, I knew that my products and my processes were each and all of them totally different, physically, chemically and patentably, from any, each and all of the products or processes described before or during the time any or all of my work was in progress, inclusive of any or all publications by Dr. Baekeland.

I will, however, briefly describe the substance called condensite which is now being manufactured and sold in the United States by the Condensite Company of America at Glen Ridge, N. J., under my patent applications pending in this country, among which is one corresponding to the Belgian patent referred to in the July number of THIS JOURNAL.

Condensite is a high-grade plastic which may be rapidly molded in its uncured state and can be hardened with or without pressure, in from one minute, more or less, to one hour, more or less, depending on the particular composition, its mass and the care with which it has been manufactured. The products, which are now being manufactured and marketed and used in the United States for more than six months last past, are each respectively of constant composition and absolutely reliable products in their molding properties.

It is adapted for molding in either open or closed molds without the necessity, as for instance in the

rubber industry, or in the manufacture of bakelite, of a vulcanizer or equivalent apparatus, in a very simple and rapid manner and the strength is so great and the contraction so small that beautifully molded objects are made and metal parts can be molded within it and without any difficulty from cracking.

Present experience shows that for practical purposes and under certain conditions, condensite is oil-proof and is acid-proof, except in the cases of nitric acid, concentrated sulphuric acid, and the strongest hydrofluoric acid. Cold or hot, dilute or strong solutions of caustic soda or caustic potash do have an action on it, and the statement on page 439 of the June issue of *THIS JOURNAL* should be read and understood in the light of the foregoing. Unfortunately, I did not have an opportunity of editing that note.

Condensite is harder and is stronger than hard rubber in tensile strength. It differs from other phenolic condensation products in several features which are of vital importance, among which the following may be mentioned: freedom from stresses due to excessive shrinkage and other causes, such as the retention of vapors due to the reaction under a compensating pressure; for all practical purposes it is non-odorous in the cured state, and nearly so in the uncured state; uniformity and reliability of manufacture; extremely high dielectric strength even when small per cents. (say 2 per cent.) of lampblack are compounded with it and the molded object is not specifically made for high tension insulation; when specifically so made, its dielectric strength is enormous.

The expression "quantitative synthesis" should be intelligible to Dr. Baekeland, but, assuming that his questioning is in good faith, I will explain that that expression is a descriptive statement of a synthetic operation in which the fate of all materials used at the beginning of the operation is accounted for at the end of the operation in contradistinction to the ordinary and usual synthetic operation in which only selected parts of the initial materials are accounted for at the end of the operation.

As to Dr. Baekeland's comment on what I have offered in my Belgian patent as to the molecular weight of one of my new products, I say that at the time I made those determinations I was fully aware of all the disturbing or possibly disturbing conditions referred to by Dr. Baekeland, but I believed then and I believe now that within the limits indicated in that patent I succeeded in overcoming those experimental obstacles. By reference to the Belgian patent it will be seen that, at the best, my statement as to molecular weight is merely a surmise and is not made as a hard and fast and rigidly proven fact.

In answering Dr. Baekeland's communication, I trust I may be pardoned for confining myself to some of the technical matters discussed therein and leaving for some other occasion those points which have their interest only from a legal or commercial point of view and which while of paramount importance to Dr. Baekeland because of his financial interest in bakelite,

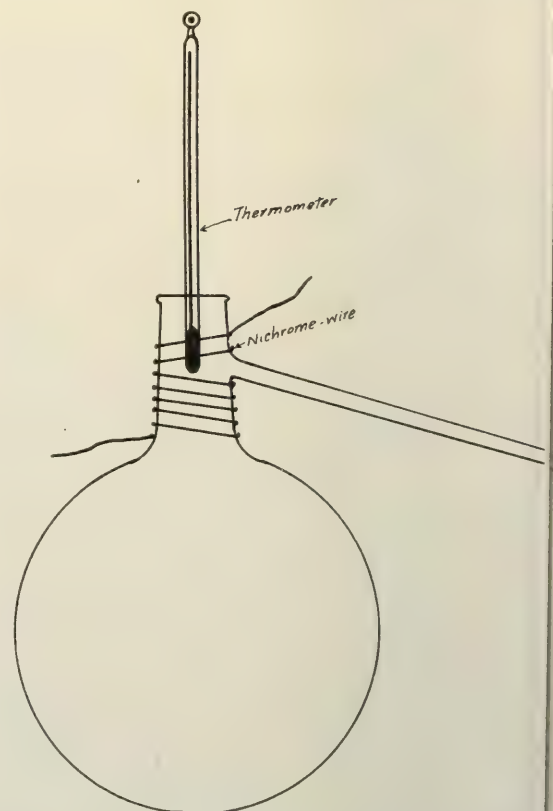
of which he is the inventor, are doubtless of minor interest to the readers of *THIS JOURNAL*.

J. W. AYLWORTH

GLEN RIDGE, N. J., July 5, 1911.

FLASK FOR DISTILLATION OF TARS.

In *THIS JOURNAL*, 3, 110, is a "Note on the Distillation of Tars Containing Water." The object of the method was to provide a means for the prevention of "bumping." Previous to the article, a method had been in use in the Laboratory of Industrial Chemistry in the University of Washington, which effectually accomplished this result. A thin sheet of a bestos paper was wrapped once around the neck of the distillation flask, and this in turn wound with a few turns of No. 30 Nichrome resistance wire. A thick covering of



asbestos was put over all and securely fastened. An electromotive force of 15-30 volts impressed on the terminals of this wire will furnish enough heat to keep the neck of the flask up to the required temperature, and in this way end any condensation which would have gone on in the neck. As a practical laboratory method, this has been tried and proved satisfactory in preventing "bumping" in the distillation of wood tar.

C. E. BROWN,
G. B. SHADINGS

UNIVERSITY OF WASHINGTON,
SEATTLE, WASH.

NOTE ON THE TWITCHELL PROCESS OF DECOMPOSING FATS.

In the decomposition of fats and oils by the Twitchell process the progress of the decomposition is followed

by titrating the free fatty acids at any stage of the operations. The percentage of free fatty acids found does not necessarily represent the percentage of decomposition of the neutral fat in the original mixture, though it is often quite close to this figure even with considerable free fatty acids present at the start. As the decomposition of the neutral fat is the object sought it is important to be able to figure its decomposition correctly.

To this end we must know:

The total fatty acids obtainable from 100 parts of neutral fat.

The true combining weight of these fatty acids.

The true per cent. of free fatty acids at the start (titrated, using true combining weight).

The true per cent. of free fatty acids in the product (titrated, using true combining weight).

With this data we can derive an expression giving us the true per cent. of decomposition of the neutral part of the mixture taken at the start.

Let x = percentage of decomposition expressed decimally, as 90 per cent. decomposition would be expressed as 0.90.

Let y = per cent. of free fatty acids in the product, also expressed decimally, as 95 per cent. would be expressed as 0.95.

F = a factor that varies with the per cent. of free fatty acids originally present.

Then $x =$
100 y — per cent. of free fatty acids originally present,
expressed as a whole number

Total fatty acids in neutral part of mixture at
start + $F y$.

In this expression y is found by titration, using correct combining weight of fatty acids. Original free fatty acids are found by titration.

Total fatty acids are neutral fat by multiplying the per cent. of neutral fat in the mixture by the per cent. of total fatty acids obtainable from such neutral fat.

F is found as follows:

100 — the free fatty acids gives the neutral fat.

The neutral fat — the fatty acids obtainable from it gives F .

An example will make the matter clearer.

Let the free fatty acids originally present be 3.84 per cent.

Let the final free fatty acids (as expressed on the final product) = 0.8996 = y .

Let the neutral fat give 0.9511 of its weight of total fatty acids.

$$100.00 = \text{Neutral fat} + \text{fatty acids (free).}$$

$$3.84 = \text{Free fatty acids.}$$

$$96.16 = \text{Neutral fat.}$$

$$91.46 = 96.16 \times 0.9511.$$

$$4.70 = F = \text{factor for } y.$$

$$\text{Then for our example, } x = \frac{100(0.8996) - 3.84}{91.46 + 4.7(0.8996)}$$

$$\text{solving, } x = 0.90$$

Decomposition = 90 per cent. of neutral fat.

It will be noticed that the decomposition is almost

the same as the amount of free fatty acids found in the final product, and for the higher percentages of decomposition this will be the case with either neutral fat to start with or a mixture containing several per cents. of free fatty acids. That it is not the case under all circumstances may be seen if we consider the original mixture to contain free fatty acids without any decomposition of neutral fat.

Where the original mixture or final product contains moisture or other substances besides the fat and fatty acids, the two latter should be considered as making up 100 per cent. of fatty matter and figured accordingly.

—W. H. LAM.

SUMMARY OF CEMENT INDUSTRY IN 1910.

The statistics of cement production in 1910, as reported by Ernest F. Burchard, of the United States Geological Survey, indicate that the cement industry ranks within the first eight extractive industries in the United States, the value of the cement produced being exceeded only by the value of the coal, pig iron, petroleum and gas, clay products, copper, gold, and stone.

The total quantity of Portland, natural, and puzzolan cements produced during 1910 was 76,934,675 barrels, valued at \$68,052,771. This was an increase of 10,244,960 barrels, or 15.3 per cent., in quantity, and of \$14,442,208, or 26.9 per cent., in value, over the figures for 1909. The increase in quantity is one of the largest ever recorded, and the fact that the increase in value was proportionately higher indicates that trade conditions were slightly more satisfactory than during 1909.

Portland cement constituted the main item in this output, the total for the year being 75,699,485 barrels, valued at \$67,506,479. This quantity is equivalent to 12,841,430 long tons, valued at \$5.26 a ton. It approximates 47 per cent. of the quantity of pig iron produced in 1910. The average price per barrel in 1910, according to the figures reported to the Survey, was a trifle less than 89.2 cents. This represents the value of the cement in bulk at the mills, including the labor cost of packing, but not the value of the sacks or barrels. The prices ranged generally between 72.7 cents a barrel in the Lehigh district and \$1.38 on the Pacific coast. While the average price for the whole country increased from 81.3 cents in 1909 to nearly 89.2 cents in 1910, with corresponding increase in the eastern, central, southern and western districts, the average price in the Pacific coast States dropped from \$1.52 to \$1.38, a decrease of 14 cents a barrel, due, no doubt, to the advent of new mills in California, the Rock Mountain States, and Western Texas, and to the increased capacity of other plants supplying the coast territory, where attractive prices have hitherto prevailed.

The number of producing plants increased from 108 in 1909 to 110 in 1910, but the total number of rotary kilns in operation decreased from 930 to 900. The figures indicate, however, that the proportion of large kilns is increasing, 471 kilns 100 feet or more in length being reported in 1910.

The Portland cement plants in the East, including plants in Pennsylvania, New Jersey, New York, and Massachusetts, produced 33,306,560 barrels in 1910, at an average price of 75 cents a barrel. The plants in the Central States—Ohio, Indiana, Michigan, Illinois, Iowa, and Missouri—produced 22,617,009 barrels, at 91 cents. The plants in Kansas, Colorado, South Dakota, Utah, Arizona, and Montana, included under "Western States," produced 7,672,369 barrels, at \$1.03. The Pacific coast plants, in California and Washington, produced 6,385,588 barrels, at \$1.38. The plants in the South,

located in Maryland, Virginia, West Virginia, Kentucky, Tennessee, Georgia, Alabama, Oklahoma, and Texas, produced 5,717,959 barrels at 94 cents.

The Barbar Asphalt Company has engaged Dr. Albert Sommer to take charge of a new department which will embrace recently developed Trinidad liquid asphalt products. Dr. Sommer until lately was in charge of the scientific development work of the Texas Company.

The next meeting of the International Association of Chemical Societies will be held on April 13th, 1912, in Berlin under the presidency of Prof. Wilhelm Ostwald.

Dr. H. E. Sawyer, formerly of the Bureau of Chemistry of the U. S. Department of Agriculture, died on July 5th at the age of 43 years.

CONSULAR AND TRADE NOTES.

THE COBALT SILVER MINES.

Since the inception of the camp in 1904, the silver mines of the cobalt district have shipped ore containing 93,275,077 ounces of silver, valued at \$48,265,236, after freight and smelting charges were deducted. During 1910 there were 33,519 tons of ore shipped by the mines, having a silver content of 29,856,069 ounces, worth \$15,375,000.

By calendar years, the production of the cobalt district was:

Year	Ore shipments, in tons	Silver content, in ounces	Value.
1904.....	158	206,875	\$ 111,887
1905.....	2,144	2,451,356	1,360,503
1906.....	5,335	5,401,766	3,667,551
1907.....	14,788	10,023,311	6,155,341
1908.....	25,624	19,437,875	9,133,378
1909.....	30,677	25,897,825	12,461,576
1910.....	33,519	29,856,069	15,375,000

This camp has in seven years produced ore of a gross value of a little over \$50,000,000. Of this sum \$30,000,000 was net profit, and there is now in sight an ore reserve conservatively estimated at \$30,000,000. The average value of the total tonnage shipped was approximately \$500 per ton, and each ton netted a profit of \$266.

KAURI-GUM INDUSTRY OF NEW ZEALAND.

In 1910, for the first time in the history of the kauri-gum industry of New Zealand, except in 1893 (a year of panic and depression in the United States), exports to the United States have been exceeded by shipments to Europe, the United States taking only 3,839 tons, as against 4,150 tons purchased by Europe. During the preceding year 5,127 tons were exported to the United States, as against 3,123 tons to Europe. As a general average, the United States in recent years has taken about two-thirds of the annual output of kauri-gum in New Zealand. Over one-half of New Zealand's total exports to the United States still consists of this gum, the exports invoiced during 1910 through the American consulate-general and agencies being valued at \$1,271,891 out of total exports from New Zealand to the United States valued at \$3,409,468. During the preceding year the value of kauri-gum exported to the United States was \$1,891,497, so that there was a decrease for 1910 of \$619,606.

SWEDISH WOOD-PULP TRADE.

The proposal of the Swedish and Norwegian wood-pulp associations to limit the production was fully approved by the members to go into effect on June 1, 1911, continuing until January 1, 1913. It is stated that the agreement calls for a reduction of at least 150,000 tons in the production of mechanical pulp for the period stated. The limitation does not apply to chemical pulp at all. Prices for both chemical and

mechanical pulp are said to be on the rise. Shipments of mechanical pulp to the United States are increasing.

Declared exports of all kinds of pulp from Gothenburg to the United States for the first quarter of 1911 aggregated \$322,282 in value, as compared to \$263,855 for the corresponding period in 1910 and \$259,066 in 1909. The following figures show the values declared for export from Gothenburg to the United States annually for the past six years:

1905.....	287,677
1906.....	269,931
1907.....	734,655
1908.....	809,736
1909.....	964,822
1910.....	1,232,474

This was chiefly dry chemical pulp, with occasional shipments of wet chemical and wet and dry mechanical pulp.

MUSSEL MUD AS FERTILIZER.

In most of the bays indenting the shores of Prince Edward Island are found extensive deposits of mussel mud, so-called locally, being organic remains of countless generations of oysters, mussels, clams, and other bivalves of the ocean and of crustaceous animals generally. The shells, usually more or less intact, are found embedded in dense deposits of mudlike substance and this combination is a fertilizer of high value and potency. It supplies lime and organic matter, besides small quantities of phosphates and alkalies. An ordinary dressing of it secures fertility in a striking manner to the poorest of most exhausted soils. The shells decay slowly, year by year throwing off a film of fertilizing stuffs. The deposits around Prince Edward Island vary from 5 to 25 feet in depth. They are taken up by dredging machines worked from rafts in summer or from the ice in winter.

SODA IN BRITISH EAST AFRICA.

The Magadi Soda Co. (Ltd.) has been formed with a capital of \$6,387,281, to acquire a 99 years' lease of and to develop the important deposit of natural soda covering an area of some 30 square miles, known as Lake Magadi, in the British East Africa Protectorate, to connect the same with the Uganda Railway by the construction of a branch line, about 100 miles long, and to build a pier and approaches thereto at or near Kilindini. The Uganda Railway administration has undertaken, on a year's notice and at its own expense, to provide all necessary rolling stock sufficient to carry 160,000 tons of soda or soda products per annum.

THE RUSSIAN PLATINUM INDUSTRY.

The Ministry of Commerce at St. Petersburg has placed before the Council of Ministers a project for regularizing the platinum industry. It is proposed to prohibit the export of platin

iferous ores from a date when Russian laboratories can take over the whole Siberian output for refining, and steps are being taken to subsidize out of treasury funds such private laboratories as require more modern equipment. Special regulations are also being drawn up by which State control of the extraction and price of the metal will be established.

COTTONSEED-OIL REFINERY IN CANADA.

The first refinery of cottonseed-oil products in Canada is that of Gunn's (Ltd.), in Toronto. The plant is equipped to manufacture a complete line of salad oils, cooking oils, and shortening composed of compounds of vegetable and animal fats and oils. The capacity is 20,000,000 pounds per annum. The com-

pany has a line of tank cars engaged in carrying cottonseed-oil in its crude state from the mills of the Southern States.

IODINE FROM CHILE.

The Domeyko iodine works in the north of Chile are said to be the largest in the world, with an annual capacity of 400,000 pounds. The total production of iodine in Chile for 1910 amounted to 1,279,150 pounds.

TIN MINING IN BOLIVIA.

The Pulacayo tin mines in Bolivia have reached the depth of 2,304 feet, and the richness of the ore increases as the mine descends. This mine has been worked for more than 300 years.

BOOK REVIEWS.

Applied Electrochemistry. By M. DE KAY THOMPSON, PH.D. 329 pp. The Macmillan Company. Price, \$2.10 net.

This is a work which is the result of the studies of applied electrochemistry by one who is well equipped with the knowledge of the theoretical side of the subject. It is intended as an introduction to applied electrochemistry for students who are already fairly well equipped with a knowledge of theoretical chemistry and electrochemistry.

Electrochemical measuring instruments are first described and sufficient detail given to permit one to make and operate the different types with a knowledge of the probable accuracy to be obtained. Frequent references to the literature are made in the case of most of the subjects taken up and these enormously increase the value of the book. Under electrochemical methods of analysis a number of interesting processes are given for determining concentration of various salts or ions through direct reading electrical measuring instruments. These are interesting as suggesting such applications to untried fields, but are admittedly not intended as representing electrochemistry now usefully applied in analysis. Such applications are still quite rare, but their comprehension by the student insures an understanding of some of the important quantitative principles of electrochemistry.

The ordinary processes of electroplating are briefly considered. Apparently in each case the best known formulae for the baths have been selected from the literature.

In the 25 pages devoted to electrolytic winning and refining of metals, a general review of the well-known processes is given, together with brief descriptions of some commercially unsuccessful processes. This scheme of discussing processes which have been only "near processes" seems a good one, as it must show the student how help may be gained from carefully considered failures.

The book makes no claim of presenting new material, but rather of forming a collection from the literature of what one would naturally call applied electrochemistry, and to this is added the most recent conceptions of theoretical electrochemistry in connection

with the subject. It certainly covers a broad field in a clear and concise manner, and the choice of processes and methods is apparently wisely made. Separate chapters are devoted, in addition, to those subjects mentioned below:

Electrolysis of Alkali Chlorides, 56 pp.

Primary Cells.

Storage Batteries.

Electric Furnaces.

Metallurgy of Iron and Steel.

The Fixation of Atmospheric Nitrogen.

Ozone.

The general impression made by the book is a good one and is what might be expected from a well trained student and teacher of the principles of electrochemistry. The illustrations are well selected and up to date.

While the application of the science is advancing so rapidly that the strictly applied portions ought to be frequently rewritten, yet the principles and the historical accounts, which are the more useful portions for the student and teacher, will remain prominent and permanent.

W. R. WHITNEY.

Drying Machinery and Practice. By THOMAS G. MARLOW. 326 pp.; 174 illustrations; 22 tables. New York: D. Van Nostrand Co. Price, \$5.00 net.

The press work and general make-up are good. It is written in a clear, concise, and logical style that can be readily understood by the ordinary reader. It is an English book and consequently deals with English practice and machinery but the fundamental principles are, of course, universal in application.

At the outset the author clearly states the reasons for drying materials, as well as the different degrees of dryness as found in practice. A brief outline of each division of the subject is taken up in a general way, followed by a detailed description of the machinery and manner of using the same, giving the results of practice, such as the power required, the amount of, and the condition of, the resultant product, so that the reader can form a correct opinion of what may be expected in practical work.

In discussing the subject of drying by evaporation,

the author shows how to determine the amount of air required to produce certain results under given conditions by the use of tables which give considerable data, yet it would perhaps have been a wise addition to have added some formulas for the complete thermodynamic analysis of mixed gases as applied to drying. Attention is called to the methods of generating and applying heat to various forms of drying apparatus, also the dangers arising from the resulting gases due to evaporation; the methods of handling the material to be dried, the action of heat upon the substance, with results obtained from practice, yet no general rule to assist in the solution of some specific problem.

The appendices containing the "Bibliography of Drying and Desiccating" and the "Glossary of Terms" are both very useful; for any one who wishes to go thoroughly into the subject of drying or to those who desire to investigate some special line, the former will be of considerable help.

In general, the information contained in the work is evidently the result of practical experience; consequently, it is of a practical nature and from that standpoint covers the ground very well, but by the addition of some national or empiric formulas the field of its usefulness would no doubt be enlarged.

C. W. THOMAS.

Practice of Copper Smelting. By EDWARD DYER PETERS. 693 pages. McGraw-Hill Book Company. 1911. Price, \$5.00 net.

The arrangement Dr. Peters has chosen for his otherwise excellent book is a very unfortunate one. In his first work, "Modern Copper Smelting," he produced one of the best books on metallurgy ever written. His two later volumes, the "Principles of Copper Smelting," and the present "Practice of Copper Smelting," are intended as parts of a whole, but the division is unfortunate, and if one is using either it is constantly necessary to refer to the other.

In the present work Dr. Peters has found it necessary to explain the theories of the different processes, but these explanations are seldom complete and the reader is referred to the "Principles." In a note on page 410 he says: "A simple, direct statement—not absolutely correct, and to be amended later when it has sunk in—may or may not make some useful impression on the average student; but an absolutely correct statement, buried in exceptions and complications, will certainly not be of any use to him." He has carried this to an extreme and frequently makes his statements so simple that they are misleading. He then repeats them, sometimes several times, in each case qualifying and getting nearer to completeness, and ends by referring the reader to the "Principles." This continual repetition has made the book as bulky as if the principles had been given fully and completely at once and does not appear to have any marked advantage over the method followed in his first work.

Aside from this defect, if it is one, the book is admirable. It starts with an account of the ores of

copper and methods of sampling. This is short but sufficient for the purpose. The next two chapters are a very condensed description of the general methods of extraction and of the behavior of ores at high temperatures. Next comes roasting; first the principles, then mechanical furnaces and heap roasting. He then takes up the blast furnace, its construction, variations, accessories and management, followed by illustrations of present practice under different conditions. Reverberatory furnaces are treated in the same manner. Then a chapter on the blast furnace *versus* the reverberatory, defining the limitations of each and showing that they are supplemental to each other rather than actual rivals. The next chapter deals with fines and the very troublesome question of how to deal with them. This chapter is particularly good and is of much value to others than copper smelters. The two following chapters deal with the converter and refining: they are treated in the same complete manner as the blast furnace and the reverberatory. Next is a short chapter on flue dust and smoke, giving a review of the recent methods of dealing with these substances. The chapter on slags is perhaps the least satisfactory of any in the book. While it contains much useful information it is too elaborate to be elementary and yet is far from complete. The concluding chapter includes such various subjects as furnace construction, reverberatories, arrangement and details of plant, hot blast stoves, smelter tariffs, costs and tables. It contains much good advice and many useful hints. The hot blast stove shown, however, is the only archaic piece of apparatus described in the book, but with such a stove it is not to be wondered at that heated blast is not popular with copper smelters.

In the preface Dr. Peters says: "Owing to the great development—I have, therefore, believed it best to introduce comparatively few illustrations of processes, but to select those from the best modern practice, and to study them in detail." This he has followed consistently, not loading the book with descriptions of obsolete methods and processes, but all his examples are from the most successful practice of the present day or are descriptions of methods that have proved satisfactory, under conditions that are unusual but still likely to be encountered at widely separated points.

He has wisely not gone at any length into the question of costs, that being so much influenced by local conditions, but gives sufficient information about quantities and kinds of materials, labor and repairs to enable any experienced metallurgist to make his own estimates.

He has confined himself entirely to the dry methods and describes these completely and well. It is a pity that the limitations of space prevented him from taking up electrolytic refining and thus completing the subject in one book. On the whole, the book is an excellent one and should be in the library of every metallurgist.

G. C. STONE.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

- The Manufacture of Starch, Dextrin and Starch Sugar.** By F. REHWALD. 8vo., 309 pages. \$0.75. Vienna, 1911. (German.)
- Yearbook of Electrochemistry and Applied Physical Chemistry.** By H. DANNEEL AND J. MEYER. Vol. XIII. L. 8vo., 497 pages. \$5.00. Halle, 1911. (German.)
- Grinding Appliances and Plants.** By CARL NASKE. \$3.75. Leipzig: Otto Spamer. (German.)
- Zinc, Cadmium, Copper and Mercury.** By A. BOUCHONNET. 8vo., 402 pages. \$1.25. Paris. O. Doin & Fils (French.)
- Systematic Handbook of Volumetric Analysis.** By FRANCIS SUTTON. 10th edition. 8vo., 613 pages. \$5.25. London: J. and A. Churchill.
- Sampling of the Coal in the Mine.** By JOSEPH A. HOLMES. *Bureau of Mines, Technical Paper 1.*
- The Escape of Gas from Coal.** By HORACE C. PORTER AND F. K. OVITZ. *Bureau of Mines, Technical Paper 2.*
- Action of Dilute Acids and Salt Solutions upon Gelatin.** By HENRY R. PROCTOR. *Journal of the American Leather Chemists' Association*, June, 1911. pp. 270-308.
- Estimation of Sulfides in Alkali Cyanid.** By E. C. ROSSITER. *Journal of the Society of Chemical Industry*. May 31, 1911. pp. 583-588.
- Testing of Creosote.** By C. EDWARD SAGE. *Journal of the Society of Chemical Industry*, May 31, 1911. pp. 588-594.
- Modification of Raschig's Theory of the Lead-Chamber Process.** By EDWARD DWERS. *Journal of the Society of Chemical Industry*. May 31, 1911. pp. 594-603.
- Recent Progress in Calorimetry.** By WALTER P. WHITE. *Metallurgical and Chemical Engineering*, June, 1911. pp. 296-298.
- Methods of the United States Steel Corporation for the Technical Sampling and Analysis of Gases.** By J. M. CAMP. *Metallurgical and Chemical Engineering*, June, 1911. pp. 302-306.
- New Studies in Geochemistry and Geophysics.** By A. BRUN. 40. \$6 00. Paris, 1911. (French.)
- Manufacture of Cement.** By J. FRITSCH. 8vo., 503 pages. \$5.00. Paris, 1911. (French.)
- Official Ethical Oils and Balsams of Fourteen Pharmacopeias.** By C. ROHDEN. 8vo., \$2.00. Berlin: Julius Springer. (German.)
- Qualitative Chemical Analysis.** By WILFRED W. SCOTT. 8vo., 176 pages. \$1.50. New York: D. Van Nostrand Co.
- Alcoholic Fermentation.** By ARTHUR HARDEN. P. 8vo., 102 pages. \$1.25. New York: Longmans Green & Co.
- Workshop Receipts.** Spon's, 4 Vols., 12 mo., 2100 pages. \$6.00. New York: Spon & Chamberlain.
- Methods for the Examination of Milk and Dairy Products.** By C. BARTHEL. Second edition. L. 8vo., 309 pages. \$1.75. Leipzig, 1911. (German.)
- Sulfur-tars.** By W. SCHEITHAUER. L. 8vo., 200 pages. \$2.50. Leipzig, 1911. (German.)
- Petroleum, its Physics, Chemistry, Geology, Technology and Production.** By C. ENGLER AND H. HOEFER. Vol. III. L. 8vo., 192 pages. \$14.00. Leipzig, 1911. (German.)
- The Phase Rule and its Applications.** By A. FINDLAY. 8vo., 372 pages. \$1.50. London, 1911.
- Textbook of Inorganic Chemistry.** By A. F. HOLLEMAN. Ninth edition. L. 8vo., 468 pages. \$2.50. Leipzig, 1911. (German.)
- Biological and Biochemical Studies on Milk.** By C. J. KONIG. L. 8vo., 193 pages. \$2.00. Leipzig, 1911. (German.)
- The Preparation of Malt and the Brewing of Beer.** By E. LEYSER. 3 Vols., L. 8vo., 193 pages. \$8.75. Leipzig, 1911. (German.)
- Metallurgy of Tungsten, with Special Reference to the Electrometallurgy, the Compounds and the Alloys of Tungsten.** By H. MEMICKE. L. 8vo., 194 pages. \$3.75. Berlin, 1911. (German.)
- Handbook of Chemico-metallurgical Analysis.** By J. HOGNON. 8vo., 155 pages. \$1.00. Paris: Gauthier-Villars. (French.)
- The Corpuscular Theory of Electricity; The Electrons and Ions.** By PAUL DRUMAU. 8vo., 168 pages. \$0.75. Paris: Gauthier-Villars. (French.)
- Metallurgy.** By W. BORCHERS. Translated. 8vo., 271 pages. \$3.00. New York: John Wiley & Sons.
- Laboratory Manual of Inorganic Chemistry.** By E. C. BINGHAM AND GEO. F. WHITE. 12mo., 147 pages. \$1.00. New York: John Wiley & Sons.
- How to Enamel.** By HOWARD M. CHAPIN. 12mo., 70 pages. \$1.00. New York: John Wiley & Sons.
- Essentials of Volumetric Analysis.** By HENRY W. SCHIMPF. Second edition. L. 12mo., 358 pages. \$1.50. New York: John Wiley & Sons.
- Introduction to Chemistry.** By WILLHELM OSTWALD. Translated. L. 12mo., 368 pages. \$1.50. New York: John Wiley & Sons.
- Technical Methods of Ore Analysis.** By ALBERT H. LOW. Fifth edition. 8vo., 362 pages. \$3.00. New York: John Wiley & Sons.
- Pumping Machinery.** By ARTHUR M. GREENE. 8vo., 703 pages. \$4.00. New York: John Wiley & Sons.
- Laboratory Manual for Food Chemists.** By A. BUJARD AND E. BAIER. 8vo., 730 pages. \$3.00. Berlin, 1911. (German.)
- Yearbook of the Sugar Industry of the Russian Empire for the Year 1909-10.** By M. A. TOLPYGIN. 8vo., 365 pages. \$3.75. Kiew, 1911. (Russian.)
- Course in Organic Chemistry.** By W. IPATJEV. 8vo., 373 pages. \$1.50. St. Petersburg, 1911. (Russian.)
- The Manufacture of Ceresin.** By B. SACH. L. 8vo., 217 pages. \$2.25. Halle, 1911. (German.)
- Laboratory Manual for the Fat and Oil Industries.** By J. MARCUSON. L. 8vo., 159 pages. \$1.50. Halle, 1911. (German.)
- Treatise on Analytical Chemistry.** By C. BLAS. Vol. III. Quantitative Analysis. 8vo., 497 pages. \$4.50. Louvain, 1911. (French.)
- Handbook of Mineral Chemistry.** By C. DOELTER. Vol. I, Part I. L. 8vo., 160 pages. \$1.50. Dresden, 1911. (German.)
- The Technology of Metals.** By M. G. JEMANGULOW. Part I. Alloys. 8vo., 321 pages. Price, \$1.22. St. Petersburg, 1911. (Russian.)
- Experimental Introduction to Inorganic Chemistry.** By H. BLITZ. Fourth edition. \$1.00. Leipzig: Veit & Co. (German.)
- Citric Acid and its Derivatives.** By W. HALLERBACH. \$1.25. Berlin: J. Springer. (German.)

Apparatus and Methods for the Sampling and Analysis of Furnace Gases. By J. C. W. FRAZER AND E. J. HOFFMAN. *Bureau of Mines, Bulletin 12.*

Briquetting Tests of Lignite. By CHARLES L. WRIGHT. *Bureau of Mines, Bulletin 14.*

Progress in the Colloid Chemistry of the Albuminoids. By HANS HANDOVSKY. 8vo., 56 pages. Dresden, Th. Steinkopff. \$0.50.

RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.

Quantitative Determination of Cantharidine in Cantharides and Tincture of Cantharides. By A. KNEIP, N. NEY AND F. REIMERS. *Archiv. der Pharmazie*, Vol. 249, Heft, 4, pp. 259-258. (German.)

Treatment of Tannery Effluents. By J. A. S. MORRISON. *Journal of the American Leather Chemists' Association*, Vol. VI., No. 7, pp. 326-342.

Grinding Wheels, their Production and Use. By W. HERMINGHAUSEN. *Stahl und Eisen*, Vol. XXXI, No. 21, pp. 830-847.

Preparation of Coal for the Market. By HENRY LOUIS. *Journal of the Society of Chemical Industry*, Vol. XXX, No. 11, pp. 662-672.

Valuation of Crude Rubber. By FRITZ FRANK. *India Rubber World*, Vol. XLIV, No. 4, pp. 364-366.

Experimental Study of Flame Standards. By E. C. CRITTENDEN. *Transactions of the Illuminating Engineering Society*, VI., No. 5, pp. 417-436.

Desiccation of Air by Calcium Chlorid. By FELIX A. DAUBINE AND EUGENE V. RAY. *Metallurgical and Chemical Engineering*, Vol. IX., No. 7, pp. 343-347.

The Rare Earths with Special Reference to the Thorium Industrie. By C. RICHARD BOEHM. *Zeitschrift fuer angewandte Chemie*, Vol. XIV., Heft 26, June 30, 1911, pp. 1203-1209.

The Principles and Practice of Cider Making. By B. T. P. BARKER. *Journal of the Institute of Brewing*, 1911, No. 5, pp. 425-451.

The Chemical Behavior and Preservative Action of Sulfites in Beer. By JULIAN C. BAKER AND F. E. DAY. *Journal of the Institute of Brewing*, 1911, No. 5, pp. 465-479.

Crude Rubber and its Valuation. By CLAYTON BEADLE AND H. P. STEVENS. *India Rubber Journal*, 1911, No. 25, pp. 1399-1406 of Supplement.

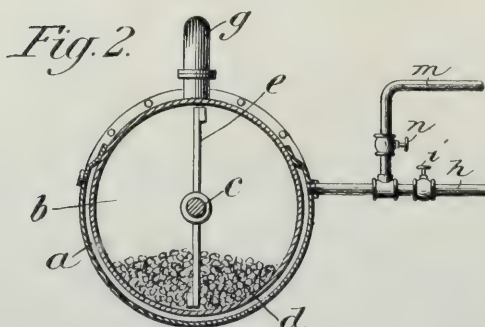
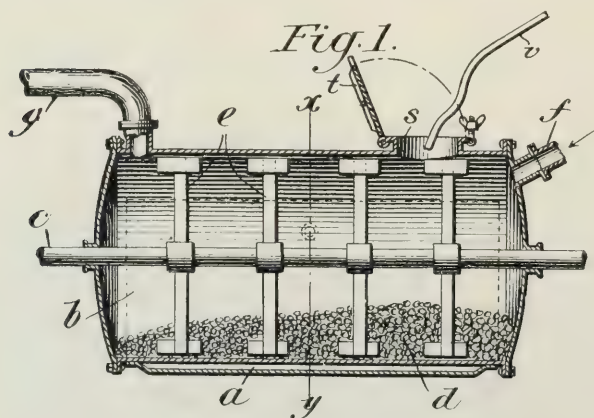
Measurement of High Temperatures. By C. T. HEYCOCK. *Journal of the Society of Chemical Industry*, 1911, No. 12, pp. 724-727.

RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

993,331. Process for the Manufacture of Formates.

This process consists in subjecting caustic alkali in lump form to the action of carbon monoxid under pressure at an initial temperature of about 100-120° C., thereby converting



the outer surface of said lumps into formate, progressively separating the formate from the outer surfaces of the lumps by agitation so as to give the carbon monoxid access to the portions within, and, after about two-thirds of the lumps of caustic

alkali have been converted into formates agglomerating the formed formates by adding about 2 per cent. of water, thereafter subjecting the mass to the further action of the carbon monoxid, and maintaining the temperature below the decomposition temperature of the formed formate during the progress of the reaction.

The accompanying illustration shows the patentee's apparatus in which he carries out the process.

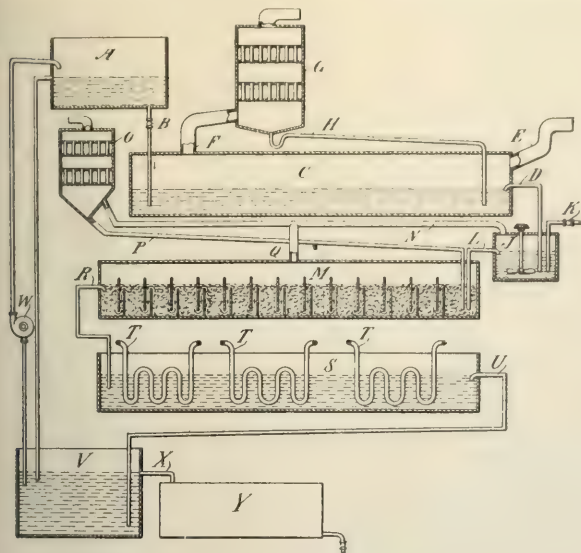
The inventor is Arnold Wiens, of Bitterfeld, Germany

992,551. Process of Producing Carbon Tetrachlorid.

In practicing this process a mixture of disulfur dichlorid and carbon tetrachlorid containing about 53 per cent. carbon tetrachlorid and 47 per cent. sulfur chlorid, at about atmospheric temperature, is allowed to flow by way of a pipe into a chlorinator C, the rate of the flow being controlled by a cock B. In the chlorinator it flows slowly from one end to the other finally overflowing at the overflow pipe D. During its passage through the chlorinator it meets and absorbs a current of chlorin, entering at E, said chlorin flowing in the opposite direction toward the outlet F. The chlorin solution overflowing at D passes into a mixer J, wherein carbon disulfid is admixed. The rate of carbon disulfid supply is controlled by a cock K. It is admitted in about the proportion of one molecule of carbon disulfid to six atoms of dissolved chlorin. The mixture now containing admixed carbon disulfid overflows continuously from the mixer by way of the overflow pipe L into the converter M. Any vapor formed in the mixer J passes by a pipe N to a condenser O, where the vapors are condensed and flows back by the pipe P into the converter M. The converter M consists of a series of compartments loosely filled with pieces of iron, for instance, sheet metal clippings, and so arranged that the liquid enters at the bottom of each compartment and overflows at the top to the bottom of the next. During its passage the iron acts catalytically and the carbon disulfid is converted to carbon tetrachlorid and sulfur chlorid. Considerable heat is evolved in the converter; with the mixture entering at 15° C. the temperature rises to around 40° C. at the exit. Any vapor formed

in M passes by way of the pipes Q and N to the condenser O where it is condensed and flows back into the converter M.

The liquid after passing through the various compartments of the converter M finally overflows through the pipe R to the cooler S where it is cooled by contact with the cooling coils T, through which cold water, brine, or cold carbon tetrachloride or other cooling liquid is circulated. The temperature of the cooling liquid, rate of flow, and surface of the coils is so regulated



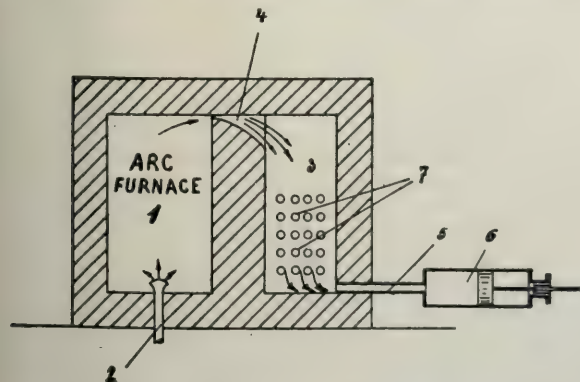
that the mixture finally overflows by the overflow pipe U at about atmospheric temperature. From U the liquid flows into the receiver V, whence it is pumped by the pump W to the reservoir A to begin its round anew.

* As the mount of carbon tetrachlorid and sulfur chlorid accumulates, a portion overflows by the overflow pipe X into a stock tank Y. Carbon tetrachlorid of a very pure form is readily separated from the stock tank mixture. The sulfur chlorid after separation is marketed as such or otherwise utilized.

The inventor is William F. Doerflinger, of New York, New York.

991,357. Process of Producing Nitric Oxid from Mixtures of Nitrogen and Oxygen and Apparatus Therefor.

This invention comprises a process wherein a mixture comprising nitrogen and oxygen, is heated to a reacting temperature, is thereafter permitted to expand without material re-



duction in temperature, additional heat being supplied during such expansion, and is finally cooled; and it also comprises apparatus suitable for carrying out the process comprising a

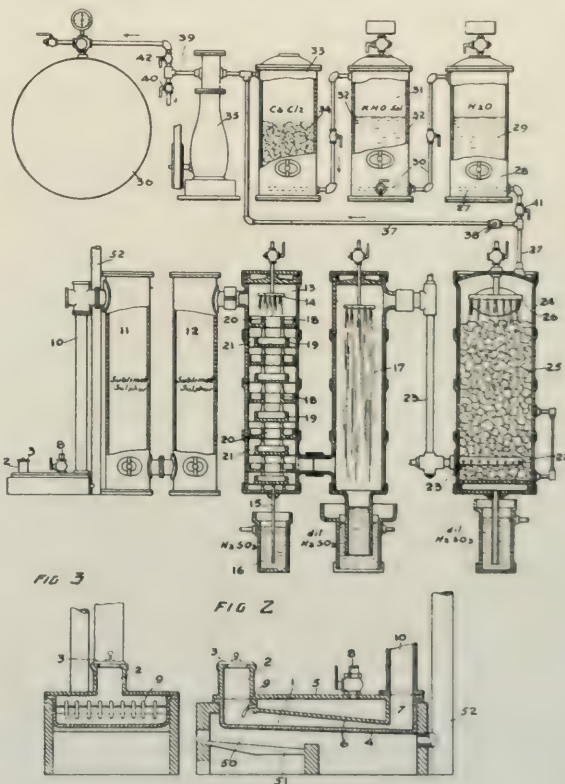
reaction furnace, an expansion chamber in communication with said furnace, means for permitting expansion of hot gases from said furnace into said reaction chamber without cooling during such expansion, special heating means being provided if desired, and means for cooling the hot expanded gases.

In applying the process to the manufacture of nitrogen oxides where gaseous mixtures containing nitrogen and oxygen are subjected to the action of an electric arc, an arc is formed and the gases introduced into it at approximately normal pressure. After treatment in the arc, the intensely hot gases are permitted to expand into a chamber in which a partial vacuum is maintained, without material reduction in their temperature. Reduction in the temperature of the hot gases may be prevented either by supplying additional heat to the gases during the expansion, or by throttling their flow into the expansion chamber. The pressure in the expansion chamber should be relatively low, and for the best results should not be over 400 mm. of mercury.

The inventor is Harry Pauling, of Gelsenkirchen, Germany, assignor to Salpetersaure-Industrie-Gesellschaft, Gesellschaft Mit Beschränkter Haftung, of Gelsenkirchen, Germany.

993,017. Apparatus for Obtaining Nitrogen from Air.

This apparatus is defined in the patent as comprising a furnace of considerable area in proportion to its height and having a top and bottom both sloping downward from the inlet to the outlet of the furnace, means for supplying sulfur and air to the inlet end of said furnace, a conduit at the outlet end of said furnace for the resulting gases, means for removing from said



gases the excess of sulfur and the sulfurous acid, a suction pump at the advance end of the conduit for drawing the air into the furnace and the gases from said furnace, and means for confining the nitrogen, substantially as described.

The inventor is Charles Blagburn, of San Francisco, California, assignor to himself, trustee.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF JULY.

For Full List of Weekly Quotations See Our Paper & Drug Reporter

Organic Chemicals

Acetanilid.....Lb.	20 1/2 @	23
Acetone (drums).....Lb.	11 1/2 @	13
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	2.53 @	2.55
Acetic Acid.....C.	1 10 1/2 @	1 8 1/2
Aniline Oil.....Lb.	14 1/2 @	14 3/4
Benzoic Acid.....Oz.	11 1/2 @	12
Carbon Tetrachloride (in drums).....Lb.	8 @	12
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	17 @	35
Carbolic Acid (in drums).....Lb.	11 1/2 @	11 1/2
Citric Acid (domestic).....Lb.	35 1/2 @	39
Camphor (refined in bulk).....Lb.	45 1/2 @	47 1/2
Dextrine (imported potato).....Lb.	5 1/2 @	7
Dextrine (domestic corn).....C.	2 55 1/2 @	2 75
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....Lb.	21 1/2 @	22 1/2
Iodoform.....Lb.	2 45 @	3.00
Oxalic Acid.....C.	7 1/2 @	7 1/2
Pyrogallie Acid (bulk).....Lb.	1 25 @	1 55
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	1 17 @	1 25
Starch (potato).....Lb.	4 1/2 @	4 1/2
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 1/2 @	5 1/4
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	30 1/4 @	30 3/4

Inorganic Chemicals

Acetate of Lime (gray).....C.	1 85 @	1 88
Acetate of Lead (brown, broken).....Lb.	7 1/2 @	8
Alum (lump).....C.	1 75 @	2 00
Aqua Ammonia (in drums) 16°.....Lb.	2 1/4 @	3
Ammonium Chloride, gray.....Lb.	5 1/2 @	6
Arsenic, white.....Lb.	1 1/2 @	2 1/2
Ammonium Carbonate, domestic.....Lb.	8 @	8 1/2
Aluminum Sulphate.....Lb.	90 @	1 1/2
Ammonium Vanadate.....Oz.	41 @	50
Bismuthine (crude, domestic).....Ton	22 00 @	22 50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 1/2
Barium Nitrate.....Lb.	5 1/2 @	6 1/2
Borax, crystals in bags.....Lb.	3 1/2 @	4
Boric Acid, crystals.....Lb.	7 @	7 1/2
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1 17 1/2 @	1.25
Barytes (prime white, foreign).....Ton	18 50 @	22 50
Blue Vitriol.....Lb.	4 1/2 @	4 1/2
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	90 @	92
Chalk (light precipitated).....Lb.	4 1/2 @	6
Cobalt Oxide.....Lb.	80 @	1 00
China Clay (imported).....Ton	11 50 @	18 00
Feldspar.....Ton	8 00 @	12 00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (in bags).....C.	60 @	85
Hydrochloric Acid (18°).....C.	1 15 @	1.75
Hydrochloric Acid (22°).....C.	1 45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 @	8 1/2
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10 00 @	11 00
Mercuric Chloride.....Lb.	81 @	84
Nitric Acid, 36°.....Lb.	3 7/8 @	4 1/4
Nitric Acid, 42°.....Lb.	4 1/2 @	5 1/2
Phosphorus.....Lb.	45 @	1 00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25

Plaster of Paris.....C.	1 50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 1/2 @	11
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2 10 @	2 15
Potassium Chlorate, crystals.....Lb.	8 1/2 @	9 1/2
Potassium Nitrate (crude).....Lb.	4 1/2 @	4 1/2
Potassium Bichromate, 50°.....Lb.	7 1/2 @	7 1/2
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	66 @	67 1/2
Salt Cake (glass-makers).....Lb.	62 1/2 @	77 1/2
Silver Nitrate.....Oz.	34 @	30
Soapstone in bags.....Ton	10 00 @	12 00
Sodium Acetate.....Lb.	4 1/4 @	5
Sodium Chlorate.....Lb.	8 1/4 @	9 1/4
Sodium Bicarbonate (English).....Lb.	2 1/2 @	3
Sodium Bichromate.....Lb.	5 1/2 @	5 1/2
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 1/2
Sodium Hydroxide, 60 per cent.....C.	1 80 @	1 85
Sodium Hyposulfite.....C.	1 30 @	1 50
Sodium Nitrate.....Lb.	1 1/2 @	1 1/2
Sodium Nitrate, 95 per cent., spot.....C.	2 12 1/2 @	2 15
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 1/4 @	10
Strontium Nitrate.....Lb.	7 1/4 @	8
Sulphur, Roll.....C.	1 85 @	2 15
Sulphur, Flowers.....C.	2 20 @	2.60
Sulphuric Acid, 60° B.....C.	85 @	1 00
Talc (American).....Ton	15 00 @	20 00
Terra Alba (American, No. 1).....C.	75 @	80
Tin Bichloride (50°).....Lb.	13 1/2 @	13 1/2
Tin Oxide.....Lb.	50 @	52
Tin Chloride (36°).....Lb.	11 @	11 1/2
Zinc Chloride (granulated).....Lb.	4 1/2 @	4 1/2
Zinc Sulphate.....Lb.	2 1/4 @	2 1/2

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 1/2
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	9 @	20
Corn Oil.....C.	5 90 @	5 95
Cottonseed Oil (crude), f. o. b. mill.....Gal.	38 @	40
Cylinder Oil (light, filtered).....Gal.	19 1/2 @	20
Japan Wax.....Lb.	9 @	9 1/2
Lard Oil (prime winter).....Gal.	78 1/2 @	85
Linseed Oil (raw, city).....Gal.	83 @	84
Linseed Oil (double-boiled).....Gal.	90 @	91
Paraffine Oil (high viscosity).....Gal.	23 1/2 @	24
Paraffine (crude 120 @ 122 m. p.).....Lb.	3 @	3 1/2
Paraffine (refined, domestic 120 @ 122 m. p.).....Lb.	4 1/2 @	4 1/2
Rosin Oil (first run).....Gal.	— @	30
Spindle Oil, No. 1.....Gal.	14 @	14 1/2
Stearic Acid (double-pressed).....Lb.	9 1/2 @	9 1/2
Sperm Oil (bleached winter) 38°.....Gal.	82 @	85
Tallow (acidless).....Gal.	64 @	66
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum [No. 1 ingots].....Lb.	20 @	21 1/2
Antimony.....Lb.	— @	9
Bismuth.....Lb.	— @	1 80
Copper (electrolytic).....Lb.	— @	12 1/2
Copper (lake).....Lb.	12 1/2 @	12 1/2
Lead.....Lb.	4 46 @	4 50
Mercury.....Lb.	61.3 @	61 5
Nickel.....Lb.	40 @	50
Platinum (refined).....Oz.	42.50 @	43 00
Silver.....Oz.	52 1/2 @	53
Tin.....Lb.	— @	43 1/2
Zinc.....Lb.	5 45 @	5 50

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EDITORIALS

THE PURE FOOD LAW.

The country has had several years' operation of the Pure Food Law, and the veriest tyro knows that it is doing things. It is natural to suppose that the five thousand members of the society have a special interest in it, because of their assistance and co-operation in its establishment and of the influence of chemistry upon its operation. Among those who have not track of its workings through the food inspection divisions and Notices of Judgment, there may be a diversity of opinion as to the details, but the attempt on the part of the government to make the law meet the conditions would probably be generally recognized. This is no attempt at a criticism of the working of the law; it is intended more as a suggestion that we chemists pay attention to this particular matter in which we may be presumed to know something and in which we at least support by our interest those who bear the burdens of seeing the law executed. It would be well for the writer a good scheme for local sections to appoint a point of inducing some one of their members to present at a section meeting a summary of the working of this law. The decisions are available through the department of agriculture. In the Notices of Judgment, now numbering over 800, one readily sees the practical operation of the law. It may be that counts of watering milk for interstate shipments, using cottonseed oil in place of olive oil, glucose for sucrose, bellows thaff where wheat and oats are being, mineral oil in turpentine, and good in nothing, do not make uplifting reading, but the general prevalence of schemes to defraud is certainly made manifest by the judgments. Those conditions of public opinion which should help cure this trouble will probably be benefitted by more general public knowledge. If a firm doing a large business is detected in shipping a quart of poison, bearing a label liquid bread,

from one State into another, does confiscation of the shipment constitute adequate punishment? If copper acetate were added to a stock of pickles to produce the same effect as the use of a copper bottle, and such pickles were improperly shipped from one State to another, what would constitute a proper fine? There are hundreds of interesting answers to such questions in the Notices of Judgment of the Department of Agriculture.

The average citizen who depends on the daily press for his information probably has a hazy notion that some one is behind a movement to prevent poisoning of the people by sodium benzoate and poor whiskey. To this knowledge it might be worth while to add a little concerning the actual working of the law. The judgments are the indicators. The average chemist may enjoy questioning whether the penalties have been too severe or not, and whether there is a need in our well advanced and civilized country for the execution of such a law. Enlightened public opinion may be assisted in its growth if our members become acquainted with the Pure Food Law.

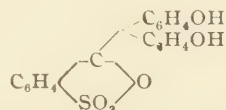
W. R. WHITNEY.

THE SUBCUTANEOUS ADMINISTRATION OF PHENOLSULPHONEPHTHALEIN AS A MEANS OF DETERMINING THE WORKING CAPACITY OF THE KIDNEYS.

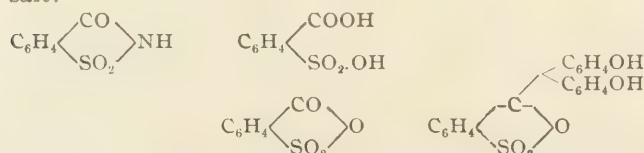
In view of the fact that the phenomena concerned in the process of secretion of urine by the kidneys are still largely a matter of speculation, any method that will accurately demonstrate the working capacity of the kidneys must be hailed with delight by the physician and surgeon.

To the chemistry of the dyestuffs, which has already furnished such valuable materials to medicine, we are again indebted for placing at the disposal of science a substance possessing most wonderful prop-

erties. To add to our pride as chemists we are able to state that the dyestuff in question was discovered by an American chemist, and that American pharmacologists established its application in medicine. This substance is phenolsulphonephthalein, first prepared by Remsen (*American Chemical Journal*, **6**, 180), and has the formula:



It is best produced from saccharine over the O-sulfofobenzoic acid, obtained from its acid ammonium salt:



John J. Abel and L. G. Rowntree (*Journal of Pharmacology and Experimental Therapeutics*, **1**, 260), who determined the pharmacological properties of the product, describe the substance as follows:

"It is a bright red crystalline powder somewhat soluble in water, more so in alcohol, insoluble in ether; its dilute alkaline solution is of a purer red than that of phenolphthalein, while a more strongly alkaline solution is purple. It is readily soluble in solutions of sodium carbonate and has a stronger avidity as an acid than any of the phthaleins hitherto examined by us.

"Solutions of the sodium salt properly made up may be injected under the skin without the slightest evidence of an irritant action. The drug may also be administered by mouth without untoward effects of any kind. Taken into the mouth as a powder it is at first slightly sweetish to the taste, then bitter and rather disagreeable. Applied in this way it stains the mucous membrane of the mouth and tongue a brilliant red which later becomes yellow and then disappears. Given by mouth to healthy human beings in doses of 0.1-0.15 gram the drug is readily absorbed and appears in the urine in the course of an hour or an hour and a half. The urine, if acid, assumes a yellow or reddish yellow color, which immediately gives place to the purple of sulphonephthalein on the addition of an alkali. After injection underneath the skin in doses of 1.6 cc. of a 5 per cent. solution it may be detected in the urine of healthy individuals within ten minutes."

It is interesting to note that the substance is absolutely harmless, manifesting no untoward effects of any kind when taken internally and causing no irritation when injected subcutaneously.

The properties which have made the use of this dyestuff as a diagnostic agent so important are that it is entirely eliminated by the kidneys, and that while it can be detected in the urine of healthy individuals within ten minutes and at the end of two hours from 60-70 per cent. of the amount administered is elim-

inated, its detection and excretion takes a much longer time in cases of renal disease.

Dr. Charles Goodman (*American Medicine*, May, 1911) summarizes the advantages of this substance as follows:

"The drug is not readily decomposed. It can be sterilized by boiling. Dose, 6 mg. injected hypodermically. Recovered in the urine as early as three minutes after injection. Within two hours from 50-70 per cent. of the drug should be recovered in the healthy state, in diseased conditions proportionately less. The drug lends itself to accurate measuring. The flow of urine excreted does not influence the amount of drug excreted. No matter how much urine, the amount of drug recovered will exactly show the index of the derangement of the kidneys. In a case of diabetes insipidus, a patient passed 1,150 cc. of urine within two hours and the drug recovered showed almost the entire amount of the dye. The presence of pus or other extraneous matters does not interfere with the proper colorimeter estimation of the amount of drug recovered. The technique is very simple. The injection is given, the time noted, the patient asked to void every five minutes in order to establish a time when the drug first appears in the urine. If there is no objection to the use of the catheter, the urine is collected for the first hour and for the second hour and the amount of the drug recovered is estimated and in that way we establish the work of the kidney."

Further observations in regard to the value of the phenolsulphonephthalein test in determining the renal function were presented by Drs. E. L. Keyes and A. R. Stevens and by Drs. J. T. Geraghty and L. G. Rowntree in two papers read before the New York Academy of Medicine, May 4, 1911 (*Medical Record* June 3, 1911).

The results of Keyes and Stevens are practically confirmatory of those obtained by Geraghty and Rowntree. The chief criticism of Keyes and Stevens is that the test serves only as an index of the total kidney capacity, and does not show how each kidney is functioning. If each ureter is catheterized separately to overcome this objection, the mere introduction of the instrument caused a diminution of the phenolphthalein output. For this reason they now make two tests, one with ureteral catheterism and the other without, and confirm the results with other tests.

In Geraghty's and Rowntree's latest study they employed intramuscular and intravenous as well as subcutaneous injections. The chief difference between the new and old method is an increase of 5-10 per cent. output during the first half hour.

There does not seem any doubt, however, as to the value of the test, for even though ureteral catheterism reduces the output of the drug, it gives the index of excretion of each kidney as a basis of comparison. On the other hand, if the catheter is not used it will show the working capacity of both kidneys together.

ORIGINAL PAPERS.

FISH OIL AS A PAINT VEHICLE.

By MAXIMILIAN TOCH.

Received July 20, 1911.

On November 3, 1910, I delivered a lecture at St. Bride's Institute, London, before the Paint and Varnish Society, on "The Newer Paint Materials," in which I outlined briefly the liquids that are used in paint materials, other than linseed oil and turpentine. A very short description was given of fish oil, but this chapter received more attention than any other part of the lecture and was widely copied throughout the United States and Europe.

The subject of fish oil demands so much attention and is so poorly understood that I take this opportunity of enlarging on the subject, not to correct any misapprehensions, but to give information which will enlighten the manufacturer and the consumer.

In the first place, we are all prone to call all oils of a fish nature "Fish oils," and I desire to differentiate between the *real* fish oils and the *pseudo fish oils*, for there are several animal oils which have fishy characteristics but which are not strictly fish oils, and these oils do not serve as good a purpose as those which are strictly extracted from fishes. Some of the fish oils—like cod liver oil—even if they were cheap enough, are not totally adapted for paint use. The animal oils which have always been regarded as fish oils, but which I call pseudo fish oils, and that are in the market and easily purchased at a reasonable price, are whale oil, porpoise oil and seal oil. All of these oils are by no means drying oils, and even if they are admixed with drying oils like tung oil and boiled linseed oil, and an additional amount of drier added, they are peculiarly hygroscopic, and after three months I have noted that although these oils may be apparently dry they become sticky when the humidity rises above 80. I append a list of oils taken out of stock, which represent standard samples, and I have given in each case the specific gravity and the iodine number, and I must say that the iodine number is a characteristic indication of the quality of a fish oil for paint purposes.

FISH OIL CONSTANTS.

	Specific gravity, 20° C.	Iodine No., Hübl, 4 hours.
No. 1 crude whale oil.....	0.9195	136.1
No. 1 filtered whale oil.....	0.9168	125.0
No. 2 filtered whale oil.....	0.9187	142.9
Cod oil.....	0.9196	147.3
Porpoise body oil.....	0.9233	132.3
Seal oil—water white.....	0.9227	143.0
<i>Menhaden oil.</i>		
Extra bleached winter.....	0.9237	150.4
Bleached—refined.....	0.9273	161.2
Regular.....	0.9249	165.7
Dark brown.....	0.9250	154.5

The specific gravities were determined with the aid of the Westphal balance.

The iodine numbers were determined according to the standard method of Hübl.

On a previous occasion I mentioned that the textbooks show the specific gravity of fish oil as approxima-

ting that of linseed oil, but in no instance have I found this to be the case within the last year, for it appears that fish oils freshly made and containing no admixture of other species, but representing the pressing of only one specie, are as a general rule below 927. The oil that gives the best and most lasting results for paint purposes is the Menhaden oil, and the winter bleached variety is the one that should be recommended. This is an oil fairly pale in color, with an iodine number of 150 or over, and with little or no fishy odor; in fact I might say that in the purchasing of fish oil for paint purposes it is well to beware of a fish oil that has the so-called characteristic fishy odor. I have not yet satisfied myself as to the cause of this odor, but as far as I have reached in my investigation I am inclined to believe it is due to phosphorus decomposition compounds. The results which I have obtained from the proper grades of fish oil—and I am glad to say there are several manufacturers sufficiently intelligent to market oils that are very desirable—warrant me in saying that fish oil in the hands of an intelligent manufacturer, and used up to 75 per cent., produces excellent results for exterior purposes. For interior purposes fish oil does not seem to be desirable, for it gives off noxious gases for a long time.

As compared with Soya bean oil, and I have continually refrained from giving any opinion as to the value of this material as an exterior paint oil, as I have not yet had sufficient time to form an opinion, it will be observed that in 1906 I published my first researches on the subject of fish oil, and I have been watching it ever since, and when mixed with linseed oil, even up to 75 per cent. of fish oil, it gives excellent and lasting results and does not show any hygroscopic properties, but when used in the raw state, particularly in conjunction with pigments which in themselves are not catalytic driers, the results are not satisfactory.

Since last year some of the enamel leather and printing ink manufacturers have adopted the use of fish oil as a medium to replace linseed oil, with excellent results, and the enamel leather which is produced, while not so high in gloss as that made entirely of linseed oil, is much more flexible and possesses an unctuousness which prevents it from cracking. But fish oil for leather purposes shows a peculiar defect, and a campaign of education will be necessary if ever this material is to be used for the manufacture of shoes or auto tops, for fish oil, particularly when it originally has a high acid number, seems to effloresce and gives an undesirable bloom to enamel leather, which, however, can be removed from the surface by the ordinary application of either benzine or a mixture of benzine and turpentine. At the same time, enamel leather is very largely used for carriage and automobile tops, and for shoes, and wherever it is used for these purposes these products are continually polished.

I might quote an analogous case of a manufacturer of chocolate who was unable to market his product,

good as it was, for the reason that the excess of cocoa butter which it contained crystallized on the surface and gave it a mildewed appearance. It was almost impossible for him to exploit his material, owing to this peculiar defect, when it occurred to him to explain to his prospective customers that he was the only man who could make chocolate that had this singular efflorescence, and that it was an indication of its quality. The public soon learned to look for chocolate that had a scum over it, and it was not very long before other manufacturers had to make chocolate of a similar appearance. The same thing might be true of enamel or patent leather. If it has a peculiar grayish bloom, due to some of the fatty acids crystallizing on the surface, it might be taken as an indication that such leather does not crack as readily as enamel made entirely of linseed oil.

The manipulation of fish oil simply amounts to this, that the manufacturers of fish oil will probably be compelled to add their own drier and their own boiled linseed oil to the fish oil and market it in that condition as a paint oil, so that the paint manufacturer may be able to buy it according to a certain specification and know he will get certain results.

We are all aware that paint made from fish oil can be applied to hot surfaces and will not blister or peel as readily as that made of linseed oil, and for this purpose—as a smoke stack paint—it is very desirable.

There is a great demand for baking japans which shall be flexible and at the same time so thoroughly baked that they adhere to the surface most tenaciously and form an excellent enamel, and for this purpose we know that the reasonable use of fish oil improves baking japans very much indeed.

We are also aware that along the seacoast, where paint disintegrates very rapidly on account of the sea air, a fairly liberal use of properly treated fish oil serves a useful purpose.

When red lead is mixed *33 lbs. to a gallon of linseed oil* it thickens up after a very short time and becomes unfit for use. A properly neutralized fish oil prevents the hardening or setting of the red lead in the package, and a paste of this material can be transported a great distance and will last many months in a fresh and soft condition.

All the samples herewith submitted and painted on steel, of the various fish oils, pseudo fish oils and linseed oil, are without the admixture of driers, and you will note that the Menhaden fish oil and the linseed oil have dried approximately the same, but the seal oil and whale oil are still sticky after two weeks. This may be an unfair test, for these other oils can be manipulated with the proper driers and they will serve a fairly good purpose, but inasmuch as Menhaden fish oil appears to be satisfactory for this test even without a drier, its superiority over the animal oils is apparent.

Menhaden oil should, of course, be used with a drier, and for that purpose the best results are obtained by means of a Tungate drier. A Tungate drier is one in which tung oil or China wood oil is boiled with a lead and manganese oxide, and when

the solution is complete this is then mixed with a properly made resinolate of lead and manganese. Such a drier becomes soluble in the oil at temperatures over 100°C ., and hardens the resulting paint very thoroughly. For fabrics, however, fish oil must be heated to a temperature of over 200°C ., and if air is injected at such a temperature the glycerides are expelled and thick oil is produced which, in conjunction with the drier just named, is equally good for printing inks. It is advisable, however, to add at least 25 per cent. of either a heavy bodied linseed oil or a raw linseed oil which does not break before the manipulation just referred to is begun.

For stacks, boiler fronts, etc., I have already pointed out on another occasion that the treatment of fish oil up to 220°C . with litharge makes a heat-resisting medium that is far superior to anything excepting China wood oil, and for both heat-resisting and exposure to the elements fish oil is superior to China wood oil.

THE EFFECT OF PIGMENTS GROUND IN LINSEED OIL.

By HENRY A. GARDNER.

Received July 21, 1911.

In a recent contribution to the technology of drying oils, Sabin¹ describes the peculiar action that various pigments have upon the drying of linseed oil. Pigments such as barytes and China clay, which have always been considered by the paint chemist as inert pigments or pigments developing no chemical action when ground in linseed oil, appeared in Sabin's test to accelerate the drying of linseed oil when ground therein, and spread out to a thin film. The writer has always contended that such action was not due to any chemical effect between the inert pigments and the oil, but rather to the physical action of such pigments in distributing the mass of oil in which they are ground and thus allowing a greater surface to be exposed to the oxygen of the air. Sabin has stated that the action of such pigments may be due to the hindering of peroxidation processes which involve the loss in weight of the oil films. The writer feels, however, that the stimulation of oxidation by catalytic or contact action may more readily account for the effect these pigments have upon the drying of linseed oil.

The point at issue seems to be whether the so-called inert pigments really have any chemical action when enveloped in linseed oil. To determine this point, the writer has conducted a series of tests which seem to conclusively prove that the pigments in question are really chemically inert and have absolutely no such action. The tests were made in the following manner:

Five grams of each of a series of commonly used paint pigments, including those of inert crystalline nature as well as the more valuable amorphous pigments which are considered more or less chemically active, were ground separately in an agate mortar, with 5 grams of raw linseed oil. The ground paste in each case was placed in a marked glass beaker,

¹ "Linseed Oil," by A. H. Sabin, *THIS JOURNAL*, **3**, 84, 1911.

and allowed to stand in a dustless section of the laboratory for one month. The oil-pigment paste from each beaker was then separately extracted with benzine to remove the linseed oil from the pigment. The benzine solutions of oil were then heated to remove the benzine and the residue of oil burned to ash in crucibles. The ash from each test was weighed, and if it ran above the percentage of ash determined on a blank sample of linseed oil (namely, 0.003 per cent.), the ash was analyzed qualitatively for metallic constituents. The following table of results shows the percentage increase in ash, as well as the constituents of ash on the various samples tested:

TABLE OF RESULTS.

Pigment in oil.	Per cent. of ash in oil extracted from oil-pigment paste.	Analysis of ash.
Raw linseed oil without pigment.....	0.003
Barytes.....	0.003
Blanc fixe.....	0.003
Silica.....	0.003
Asbestine.....	0.005
China clay.....	0.007
Whiting.....	0.008
Chrome yellow.....	0.025	Lead oxide (PbO)
Lithopone.....	0.031	Zinc oxide (ZnO)
Prussian blue.....	0.032	Iron oxide (Fe ₂ O ₃)
Sublimed white lead.....	0.033	Lead oxide (PbO)
Zinc oxide.....	0.105	Zinc oxide (ZnO)
Corroded white lead.....	0.116	Lead oxide (PbO)
Red lead.....	0.2112	Lead oxide (PbO)

Observation of these results shows that pigments such as barytes, blanc fixe, and silica have no chemical action on the linseed oil. The results on asbestine and China clay also are negative, the extremely slight increase in amount of ash from these samples probably being due to traces carried over mechanically into the oil mixture, the last named pigments being more fluffy and difficult to separate from oil. Slight action seemed to be apparent in the case of whiting, a pigment somewhat alkaline in nature. A sponger test might have shown this pigment to have possessed still greater action. Sublimed white lead, a paint pigment considered of great value by the paint grinder, for use with tinted paints which are liable to destruction when ground with alkaline pigments, showed but little action on the linseed oil. Corroded white lead, which is well known to be quite alkaline in nature, showed considerable action, indicating that the formation of lead linoleate or some other organic lead compound takes place when this pigment is ground in oil. Zinc oxide and lithopone, the latter pigment containing 30 per cent. of zinc sulphide, both indicated action on the oil. Chrome yellow (chromate of lead) showed some action, as did also Prussian blue, the ash from the last named pigment showing a heavy percentage of iron oxide. Red lead showed a most astounding gain in these tests, chemical action of the pigment on the oil being apparent soon after the tests were started, as shown by the formation of a hard cake with the linseed oil. The raw linseed oil which was used in these tests had an acid value of 1.84 which is very low. The neutralization of this free fatty acid by some of the

alkaline pigments used may account for part of the increased percentage of ash. It is the writer's belief, however, that in many cases the pigments, and more especially the basic pigments, had a direct saponifying action upon the glycerides of the oil.

Summing up the results, it is fair to say that the inert pigments so-called are really inert chemically, and that the lead and zinc pigments are chemically active. It would seem advisable, therefore, to use in paints made of the chemically active pigments a moderate percentage of the inert pigments, so that any marked saponification would not take place. The saponification of oil by either lead or zinc pigments is apt to result in early disintegration, as shown by exposure tests.¹ These same tests have proved that marked saponification may be prevented by the use of moderate percentages of the inert pigments.

THE INSTITUTE OF INDUSTRIAL RESEARCH,
WASHINGTON, D. C.

CUPFERRON: ITS USE IN QUANTITATIVE ANALYSIS.

By OSKAR BAUDISCH AND VICTOR L. KING.

Received July 24, 1911.

Under the name "Cupferron" one of us (O. B.) introduced the ammonium salt of nitrosophenylhydroxylamine, $C_6H_5(NO)ONH_4$, into quantitative analysis as a precipitant for cupric and ferric ions. By means of cupferron, iron and copper may be separated very rapidly and exactly, not only from one another but also from almost all the other metals. The new method exceeds in elegance, simplicity, and rapidity of operation all the methods known up to the present time for the separation of iron and copper, and has already met with great favor in technical chemical analysis in factories and mining and metallurgical plants.

The advantages of precipitating with cupferron are as follows:

I. Iron and copper are precipitated from solutions strongly acid either with mineral or acetic acids. The precipitated iron and copper salts may be very easily and thoroughly washed free from the chlorides, nitrates, sulphates, etc., of any other metals which may be in solution.

II. The precipitates settle rapidly and may be filtered off without loss of time.

* III. The separation of the iron from the copper is accomplished simply by washing the precipitate on the filter with dilute ammonium hydroxide solution. The ferric salt is completely insoluble and remains on the filter.

IV. The iron salt is readily soluble in ether, chloroform, acetone, etc., and may be dissolved, on the filter, away from any other metallic salts such as Pb, Ag, Hg, Sn salts, which may have been simultaneously precipitated.

The particular value of the new method lies in the fact that by its means iron may be rapidly separated from aluminum, manganese, chromium, nickel and cobalt. The "cupferron" method has been thoroughly

¹ See *Bulletins* 26 and 28, Paint Mfrs' Assn. of U. S.

tested from many sides, and the work of H. Nissenson, A. Biltz and O. Hödthe, and Fresenius quite confirm our results.

Cupferron will undoubtedly find extensive application in the quantitative analysis of widely different materials, for it has also been discovered that titanium, cerium, and zirconium may be quantitatively precipitated from acid solutions by it.

An example showing the application of the method to a manganese ore may be of value.

Dissolve 5.0 grams of the finely pulverized ore in 60 cc. of conc. HCl, oxidize the iron with KClO_3 , and after expelling the chlorine, dilute to 500 cc. with water. Pipette out 25 cc. into a beaker and add 20 cc. conc. HCl and 100 cc. cold distilled water. Allow a solution of about 3.0 grams of cupferron in 50 cc. of cold water to flow in a fine stream down the side of the beaker, with constant stirring. A brownish red, partly amorphous, partly crystalline precipitate separates out. As soon as a drop of the reagent causes the formation of a snow-white crystalline precipitate, all the iron is down. For certainty's sake add an excess of the reagent, stir well and filter off with suction. In case the last particles of the precipitate cling tenaciously to the beaker, add a little ether to loosen them, and then remove the ether by adding a little boiling water. In this manner it is possible to quantitatively transfer the precipitate to the filter. The precipitate is now washed with cold water until the filtrate is no longer acid with the mineral acid used. Manganese may be determined in the filtrate. The precipitate is now washed twice with dilute ammonia (1 vol. conc. NH_4OH to 1 vol. H_2O) in order to remove the excess of reagent. Wash once more with cold water and fold the wet paper and precipitate together and dry in a weighed platinum or porcelain crucible with a small flame. Then cover the crucible and heat until no more inflammable gases are evolved and then ignite to Fe_2O_3 , cool and weigh.

I. Substance 5.0 grams $\frac{25}{500} = \frac{1}{20}$ taken Fe_2O_3 0.0330
= 13.2%.

II. Substance 5.0 grams $\frac{25}{500} = \frac{1}{20}$ taken Fe_2O_3 0.0331
= 13.2%.

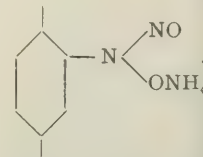
The analysis requires about $1\frac{1}{4}$ hours, but without inconvenience a number may be simultaneously carried out.

PREPARATION OF CUPFERRON.

Sixty grams of nitrobenzol, 1000 cc. of distilled water and 30 grams of NH_4Cl are thoroughly stirred up in a wide-mouthed bottle with an efficient stirring apparatus until a milky emulsion is formed. Into this emulsion (constant stirring) add 80 grams of zinc dust (the amount depends on the quality) in very small portions at a time. During the addition of the Zn dust the temperature must be kept between 15° and 18° C. This may be accomplished by simply throwing pieces of ice into the rapidly whirling liquid from time to time. Continued vigorous stirring and the keeping of the temperature within the pre-

scribed limits are the essentials which determine good yield. The reduction is continued until the odor of nitrobenzol vanishes. The time required for the reduction depends on the value of the zinc dust. It usually takes half an hour to reduce 60 grams of nitrobenzol. The white zinc hydroxide is now filtered off with suction and the filtrate cooled to 0° C. with ice, and ordinary salt (NaCl) is added to saturation. In a little while a thick mass of snow-white crystals forms. Filter off right away with suction and dry the crystals between filter paper. The yield of phenylhydroxylamine is usually about 70-85 percent of the theory. As phenylhydroxylamine solutions are vigorous skin poisons and may pass through the unbroken skin into the blood, the hands should be washed with water and alcohol in case they come in contact with such solutions.

The freshly prepared phenylhydroxylamine is dried for an hour between filter paper and then dissolved in 300-500 cc. of commercial ether. The ether solution is filtered through a dry filter and cooled to 0° C. Into this cold solution dry ammonia gas is passed for about ten minutes and then add somewhat more than the theoretical amount (more than 1 mol.) of fresh amyl nitrite all at once. The clear solution will suddenly get hot and the entire vessel will be filled with snow-white crystals of the ammonium salt of nitrosophenylhydroxylamine,



The brilliant snow-white crystals are filtered off with suction, washed with ether, and dried between filter paper. They are then to be placed in a well-closed bottle with a small piece of solid ammonium carbonate.

The salt prepared and preserved in this manner will be found a welcome and thoroughly satisfactory precipitating and separating agent for copper and iron in any busy laboratory.

UNIVERSITY OF ZURICH,
SWITZERLAND, July, 1911.

THE DETERMINATION OF MANGANESE IN VANADIUM AND CHROME-VANADIUM STEELS.¹

By J. R. CAIN.

Received May 27, 1911.

Watters² has recently described a method for determining manganese in steels containing chromium and tungsten which eliminate the errors caused by using the bismuthate method on such steels, owing to the oxidation of some of the chromium by the bismuthate. The steel is dissolved in sulphuric acid and oxidized with nitric acid, the solution nearly neutralized and the chromium and iron are precipitated with an emulsion of zinc oxide. An aliquot is filtered off, nitric acid added, and the manganese determined.

¹ Published by permission of the Director of the Bureau of Standards.
² *Met. Chem. Eng.*, **9**, 244 (1911).

by the bismuthate method as usual. This method is very similar to one which the writer devised and has used for this class of materials. There is very little choice between the two, apparently, inasmuch as the time consumed, degree of accuracy, etc., is about the same in each case. However, the method to be described might give better results than that of Watters on high vanadium products, inasmuch as the vanadium in such cases might not always be completely precipitated by his method and this would cause high results. Watters' method was tested as to this point with the Bureau of Standards chrome-vanadium standard, containing about 1.32 per cent. of chromium and 0.20 per cent. of vanadium, and no vanadium was found in the filtrate with the manganese. The percentage of manganese in the standard was found to be identical by the two methods.

It has already been shown¹ that large amounts of chromium and vanadium are completely precipitated from solutions of steel without coprecipitation of manganese, provided the iron is kept mainly in the ferrous condition while the solution is being boiled with the precipitant. To carry out the method for manganese, 1 or 2 grams of steel are dissolved in sulphuric acid (10 per cent. by volume), observing the precautions given in the last-quoted paper, and the chromium and vanadium precipitated by cadmium carbonate as described therein. To the filtrate from this precipitate add 25 cc. of concentrated nitric acid and boil till free from fumes. Cool, oxidize with bismuthate, filter through asbestos, reduce with a measured excess of ferrous solution and titrate as usual.

The method is quite rapid, and its use, or the use of similar methods which eliminate chromium and vanadium during the bismuthate oxidation, seems called for, inasmuch as the results of the cooperating analysts on the above standard were several hundredths of a per cent. high where the bismuthate method was used. Further, the Ford-Williams method also gives high results, apparently due to occlusion of chromic acid. Some precipitates of manganese obtained by the Ford-Williams method from the chrome-vanadium standard were dissolved in sulphuric acid, neutralized with cadmium carbonate and boiled. The precipitate showed appreciable amounts of chromium when dissolved in nitric acid and oxidized with potassium chlorate. A bismuthate determination of manganese in the filtrate gave a result agreeing with the determinations by the method of Watters and that of the writer.

BUREAU OF STANDARDS, WASHINGTON.

ON THE SURFACE TENSION OF MOLTEN GLASSES.

By EDWIN WARD TILLOTSON, JR.

Received June 16, 1911.

Surface tension has been, up to the present time, one of the properties of a glass or enamel of which a comparatively small amount of information is at hand. Owing to the lack of convenient methods for its de-

termination it has been impossible to measure its value and the characteristic effects upon it of each constituent of the glass. This paper is a description of a simple, convenient, and fairly accurate method whereby the surface tension of glasses may be compared.

The method is a variation of that commonly used in the case of liquids, in which the surface tension is calculated from the weight of a drop falling from a tube or a surface of definite size. This method was used by Quincke² for determining surface tension of easily fusible metals, and a modification of it for those having a high melting point. In the latter case, small metallic rods or wires were lowered vertically into the horizontal flame of a blast lamp. From the weight of the drop which was formed and which fell, and the diameter of the wire, the surface tension was calculated by means of the following equation,

$$W = 2\pi rT,$$

in which T is the surface tension, W is the weight of the drop, and $2r$ is the diameter of the rod. Quincke applied this method to a large number of elements and salts, and recorded one experiment with glass fibers. The method has, however, not been extensively used since it is not extremely accurate, but it is useful in instances where other methods are not applicable, especially where simple and rapid measurements are to be made.

The ability of this method to give absolute values for the surface tension is doubtful. At first sight it would appear that the weight of the drop increases until it just overcomes the upward pull of the surface tension, becomes detached and falls. If the problem were as simple as that, the equation given above would hold and the weight of the drops would be proportional to the diameter of the rod, or, in the case of liquids, to the diameter of the tube from which they fall. Tate stated³ this as a law, but Lord Rayleigh showed⁴ that when water is allowed to drop from various sized glass or metallic tubes, the weight of the drop increases relatively faster than the diameter of the tube up to a certain point, when the weight of the drop remains constant no matter how large the tube or surface from which it falls. Lord Rayleigh also pointed out that the weight of the drop of water is influenced by a number of factors, such as the difference in pressure within the liquid drop from the atmospheric pressure, the physical character of the surface from which the drop is suspended, and the relation of the inner to the outer diameter of the tube. It would seem, therefore, that if metallic or glass rods or fibers were used the last two factors, at least, would be eliminated.

In the experiments described in this paper the glass fibers were lowered in a vertical position with the aid of the machine shown in Fig. 1. In this figure, A is a $3/4$ -inch iron rod 30 inches long, supported by an iron plate 8 inches in diameter and $1/2$ inch thick, which is secured firmly to the table. B is a $1/2$ inch iron rod,

¹ *Pogg. Ann.*, **134**, 356 (1868). *Ibid.*, **135**, 621 (1868).

² *Phil. Mag.*, **27**, 176 (1864).

³ *Ibid.*, [5] **48**, 321.

⁴ *This Journal*, **3**, 476 (1911).

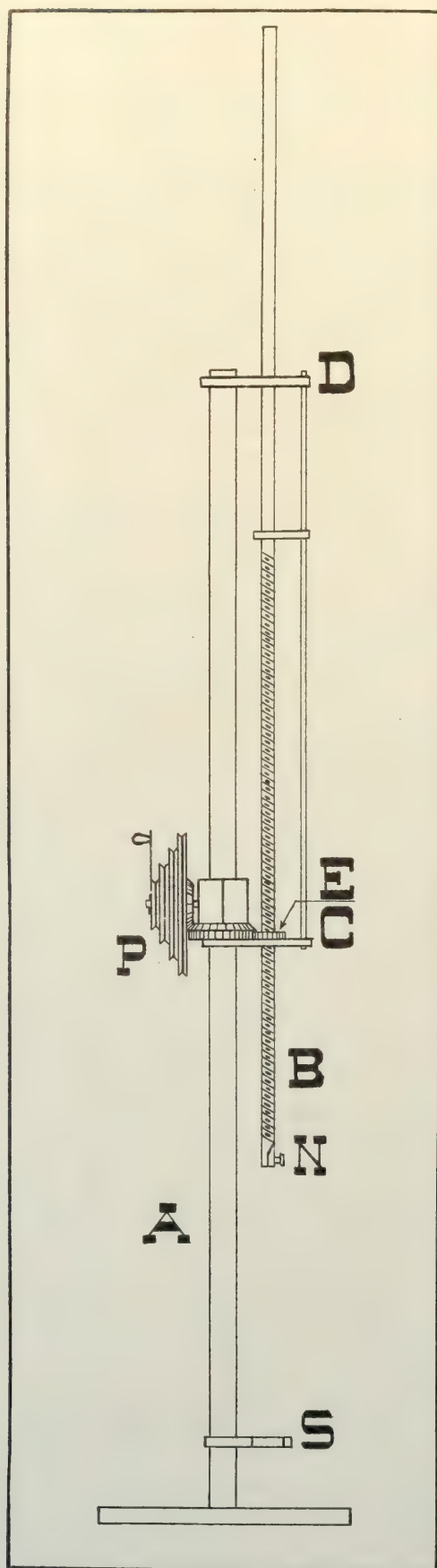


Fig. 1.

passing through the guides C and D and threaded for one-half of its length. It is raised and lowered by the threaded gear wheel E, which is actuated through gears by means of the pulley P. The lower end of B is split, forming a clamp adjusted by the milled head N. The glass fiber is held in this clamp and is kept from swinging by a loop of wire held on the stage S, which is above the blast lamp. The drops of glass were caught in a porcelain dish beneath.

Figs. 2-7 show the results obtained with a variety of silicate glasses. The approximate composition of these glasses expressed in equivalents are as follows:

- A. SiO_2 75.3 per cent., CaO 4.4 per cent., Na_2O 20.3 per cent.
- B. SiO_2 56.1 per cent., P_2O_5 3.7 per cent., BaO 10.2 per cent., CaO 17.4 per cent., Na_2O 10.7 per cent., K_2O 2.0 per cent.
- C. Composition was not definitely known, except that it contained large percentages of lead and boric oxides.
- D. SiO_2 80.1 per cent., BaO 4.7 per cent., Na_2O 15.2 per cent.
- E. SiO_2 71.4 per cent., BaO 11.4 per cent., Na_2O 17.2 per cent.

F. A beaker of Jena laboratory glass.

In the figures given the ordinates represent the weight of the drop expressed in grams and the abscissas the diameter of the fiber in millimeters. If Tate's law were correct, a straight line would be produced, *i. e.*, the weight of the drop would be directly proportional to the diameter of the fiber. It is evident from the results obtained that this is not the case, since for larger fibers the weight of the drop is greater than this law demands. If, however, an empirical factor, proportional to the area of the cross section of the fiber, be introduced, a curve may be obtained which closely approximates the experimental results. Since this new factor is proportional to the areas of the cross section or to the square of the diameter, it is evidently due to the cohesive power which exists throughout the molten glass as distinguished from the phenomena appearing at the surface. Before the drop can fall this cohesion, in addition to the surface tension must be overcome. The weight of the drop is therefore increasingly greater with the larger fibers. The continuous curves which are shown in the figures are calculated from the following equation,

$$W = a \cdot D + \beta \cdot D^2,$$

in which W is the weight of the drop in milligrams, D is the diameter of the fiber in millimeters, and a and β are constants. This equation was derived by Quincke¹ from one given by Karmarsch and was employed for calculating the surface tension of solids. However, he did not apply it to his results with molten substances. It must be remembered that, while this equation appears to satisfy the condition for small fibers of glass, it cannot be considered to be an absolutely general equation. For, as Lord Rayleigh found in the case of drops of water, there will doubtless be a limit to the size of rod, above which the drops will all be of the same size.

¹ *Loc. cit.*

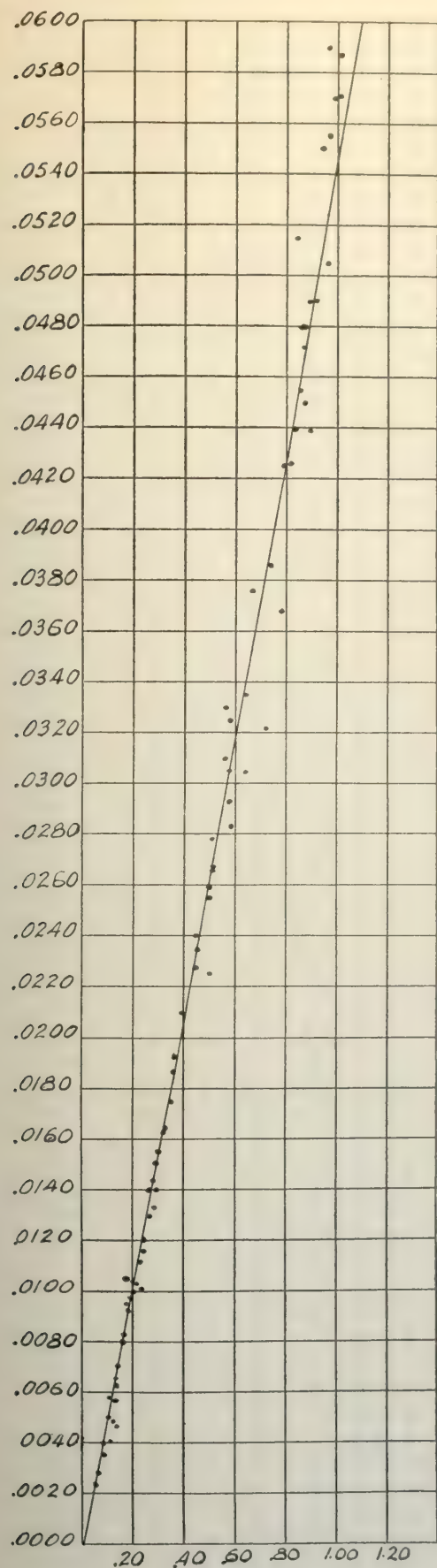


Fig. 2.

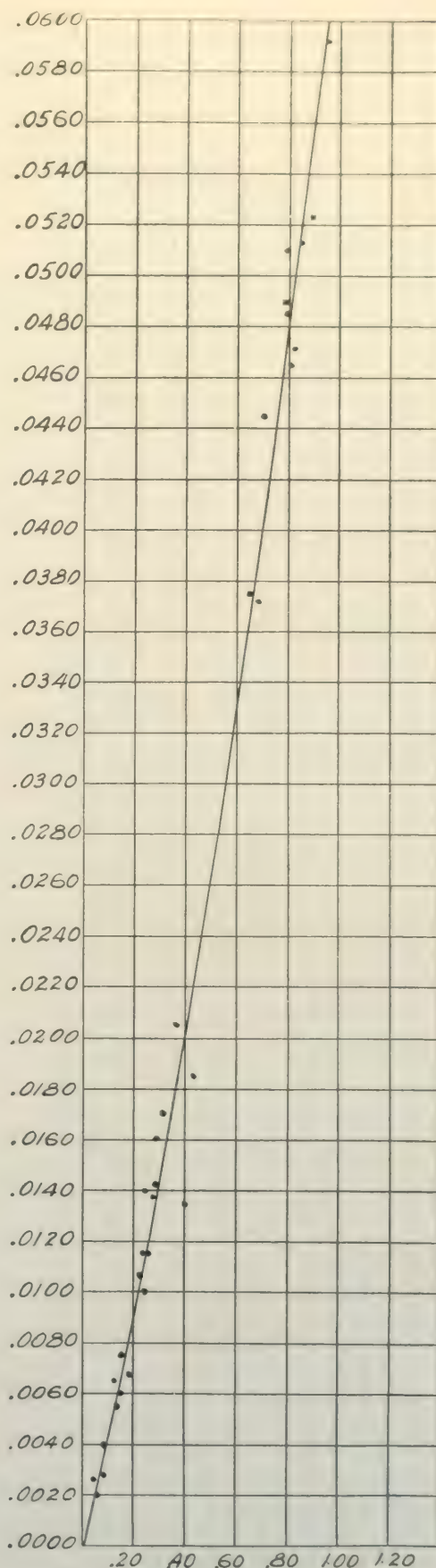


Fig. 3.

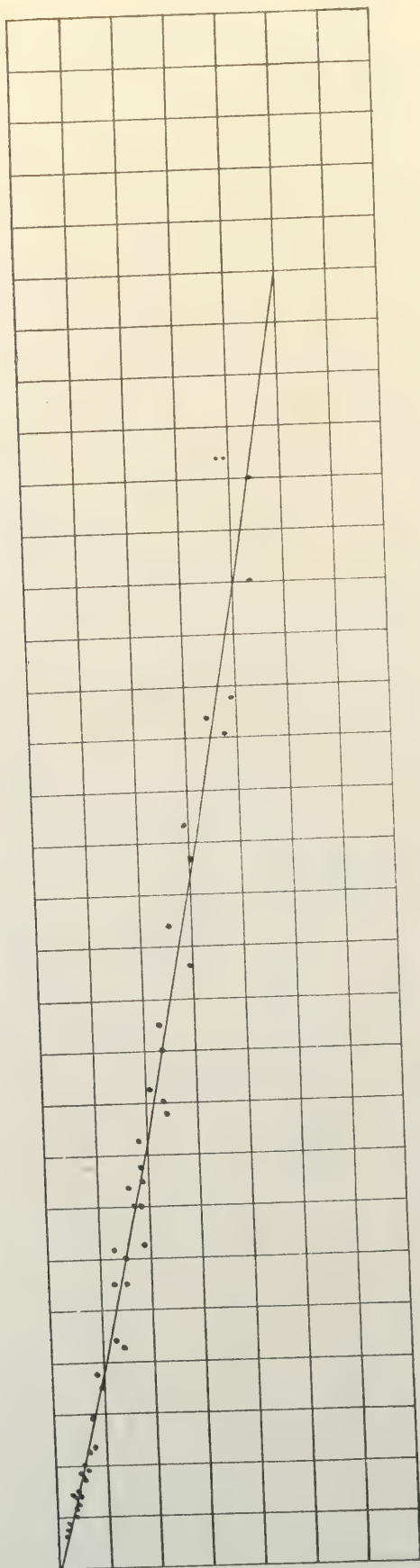


Fig. 4.

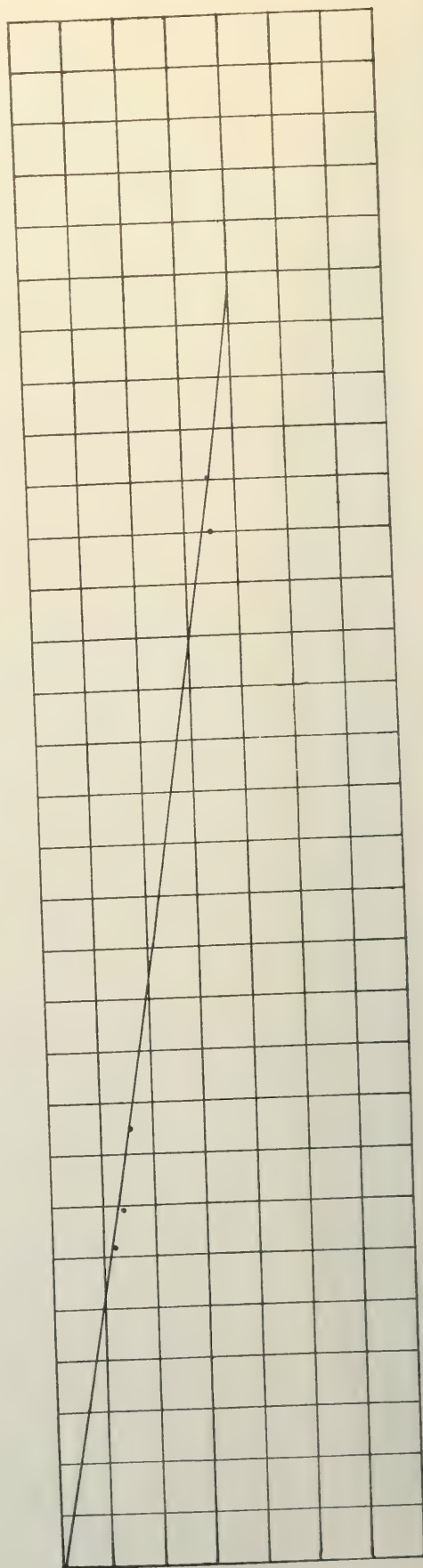


Fig. 5.

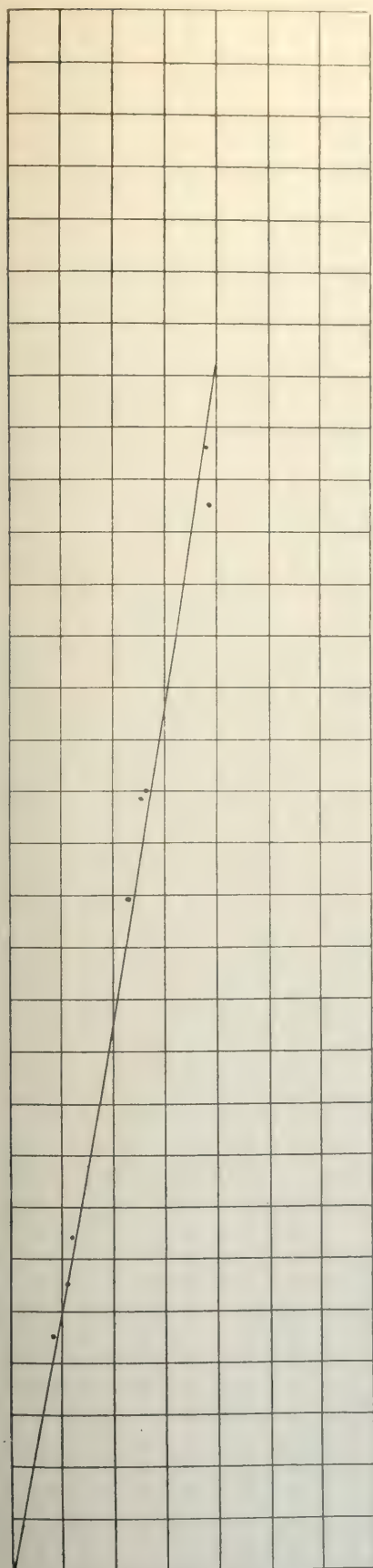


Fig. 6.

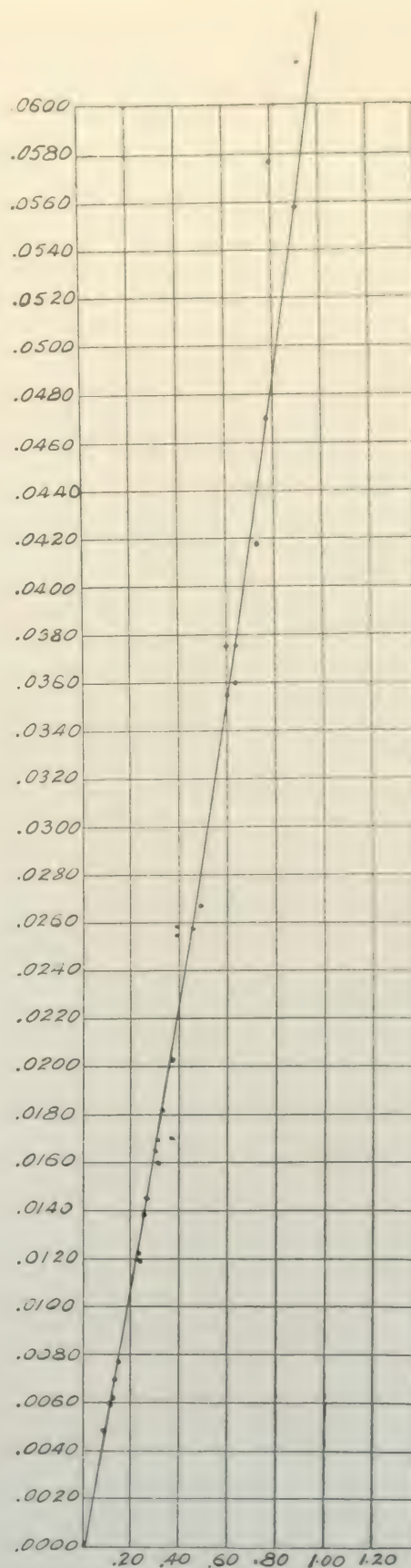


Fig. 7.

In the expression given above, a is a factor proportional to the surface tension, and from which the surface tension may be calculated, as shown by the following considerations: From the equation $W = aD + \beta D^2$ it is evident that the forces in action at the moment when the drop falls, consist of the mass of the drop, which, under the influence of gravity, acts downwards; the surface tension, proportional to the diameter (circumference) of the fiber, which acts upwards; and a third force, proportional to the square of the diameter, which also acts upwards. The weight of the fallen drop is therefore resolvable into two factors, one of which, aD , is characteristic of the surface tension. If this fraction of W be denoted by W' , we have $W' = aD$. Since the surface tension is to be recorded in dynes, the relation between the several variables is expressed by the following equation: $9.8 W' = \pi DT$ in which T is the surface tension, 9.8 is the value in dynes per centimeter of 1 mg. acting at right angles to a line 1 mm. long, and in which W and D are expressed in milligrams and millimeters respectively. By eliminating W' and D in the last two equations, and solving for T we find: $T = \frac{9.8a}{\pi}$.

Table I gives the summary of results obtained. Column 1 shows the glass used, column 2 values of a , column 3 values of β , and column 4 the value in dynes per centimeter of the surface tension as calculated from a .

TABLE I.

Glass.	a .	β .	T .
A.....	50.0	4.5	156.0
B.....	40.0	25.0	125.0
C.....	35.0	15.0	109.0
D.....	50.0	15.0	156.0
E.....	46.0	15.0	143.0
F.....	53.0	10.0	165.0

It must be remembered that these values obtained for the surface tension are probably not the absolute values, for, as Lord Rayleigh showed, in the case of water, this method gave values only slightly greater than one-half of the true value. The value of this method lies in the facility with which surface tension of two glasses may be compared, and it is not improbable that an empirical factor, such as Lord Rayleigh used, may be employed when it is desired to know the true surface tension. From the results of Table I, it is evident that glass with higher percentages of silica show the higher surface tension, and also that lead and boric oxides tend to decrease surface tension. It appears also that silicates differing widely in composition do not give extremely different values for the surface tension.

In employing this method for the determination of the surface tension of borate glass several difficulties were encountered. It was almost impossible to draw large fibers with circular cross sections. Experiments were therefore usually limited to fibers smaller than 0.6 of a mm. in diameter. The results obtained with the same size of fiber were not so concordant and showed in general a greater divergence from the theoretical straight line than those obtained with

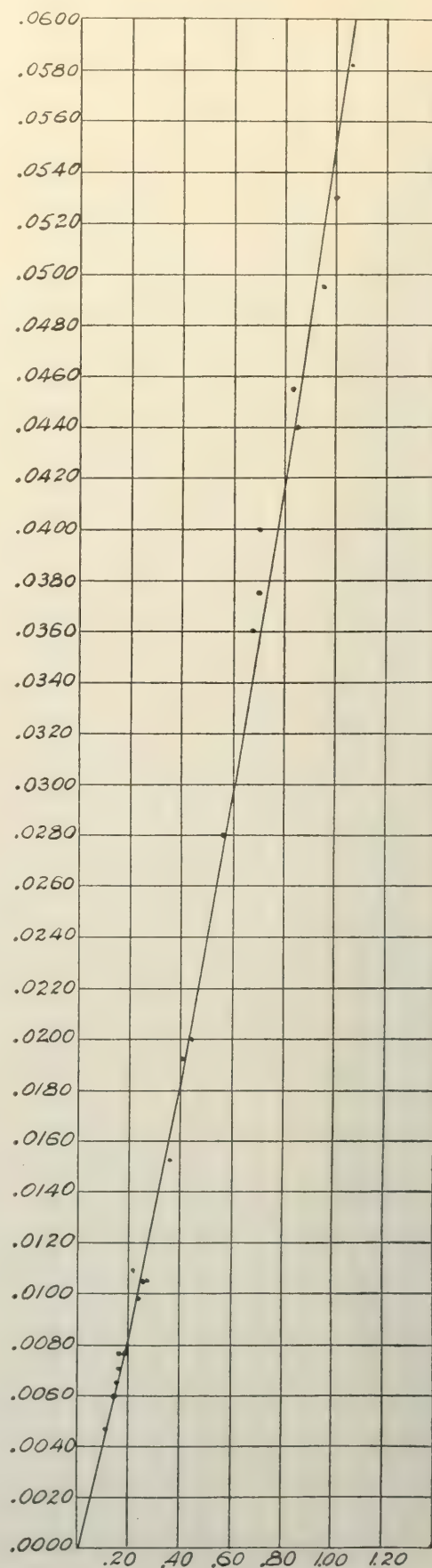


Fig. 8.

silicates. Fig. 8 shows a typical experiment. In Table II is shown the composition of glasses employed and the results obtained.

and it has been shown that for a variety of silicate glasses the surface tension lies within not very wide limits. Borate glasses possess a surface tension which

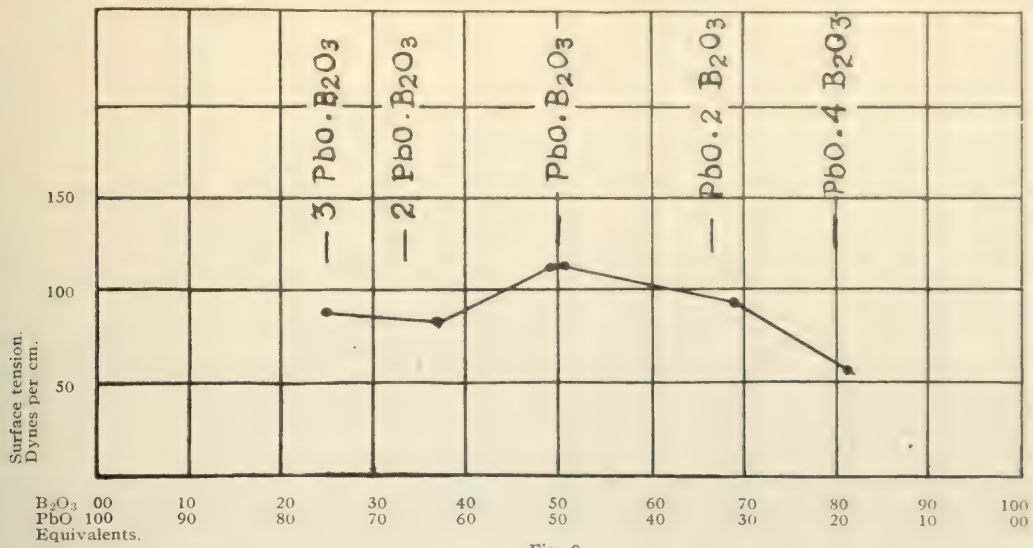


Fig. 9.
is lower than that of the silicates and which is markedly different for the several lead borates.

TABLE II.

No.	B ₂ O ₃ Equiv.	BaO Equiv.	PbO Equiv.	Na ₂ O Equiv.	α.	β.	T dynes per centi- meter.
1.....	66.7	33.3	38.0	15.0	118.0
2.....	72.8	27.2	34.0	15.0	116.0
3.....	62.1	..	9.7	28.2	34.0	15.0	106.0
4.....	59.0	..	16.7	24.3	30.0	15.0	94.0
5.....	81.1	..	18.9	..	19.0	..	59.0
6.....	68.1	..	31.9	..	31.0	..	96.0
7.....	50.7	..	49.3	..	37.0	15.0	115.0
8.....	49.1	..	50.9	..	37.0	15.0	115.0
9.....	37.2	..	62.8	..	28.0	15.0	87.0
10.....	25.3	..	74.7	..	29.0	15.0	90.0
11.....	80.0	20.0	22.0	15.0	69.0
12.....	78.0	22.0	25.0	15.0	78.0
13.....	65.5	34.5	40.0	15.0	125.0

Although these data are not complete, they bring out some interesting points. The values of β are the same for all the glasses in which enough measurements were made to determine the nature of the curve. The addition of boric oxide to borax, as shown in Experiments 1 and 2, lowers the surface tension. The addition of lead borate has the same effect, as shown in Experiments 1, 3 and 4. In Experiments 11, 12, and 13, in which barium borates were used, an increase in amount of boric oxide also causes a decrease in surface tension. On comparing these with Experiments 5-10, in which lead borates were used, we find boric acid showing the same effect when present in more than one molecule of B₂O₃ to one of PbO. In glasses which contain less than one molecule of B₂O₃ to one of PbO the surface tension behaves irregularly, showing in general a lowering of the surface tension with a decrease in the amount of boric oxide. Further work will be necessary to determine whether the surface tension may be relied upon to indicate definite compounds in a glass. The series of lead borates, as given above and plotted in Fig. 9, is sufficient to show that the presence of compounds has considerable influence on surface tension of the glass. The purpose of this paper has been to bring forward a simple and rapid method measuring the surface tension of certain high-melting substances, especially glasses. A number of experiments have been recorded

DEPT. INDUSTRIAL RESEARCH,
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A RAPID AND ACCURATE METHOD FOR THE ANALYSIS OF WHITE METALS.

By J. C. BENEKER, Metallurgist, Cincinnati Metal Products Company.

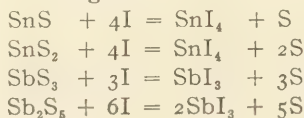
After investigating and trying many methods for the analysis of bearing and type metals, I have devised a composite scheme which embodies the best features of other researches and several ideas which I believe are original. The method is rapid and at the same time quite accurate.

Dissolve 1/2 gram of the fine drillings in a mixture of 25 cc. HCl + 5 cc. HNO or 25 cc. HCl saturated with liquid bromine (not bromine water), warm on the steam bath and add about one gram tartaric acid to hold up the antimony. Dilute with hot water to about 400 cc. and slowly add an excess of a solution of NaOH. Now add an excess (about 20 cc.) of a 10 per cent. solution of Na₂S. This is made by saturating half of a 10 per cent. NaOH solution with H₂S and then adding the other half. Allow to settle and filter by decantation a couple of times, using hot, dilute Na₂S solution for washing. Transfer the precipitate to the filter and wash with a hot, dilute Na₂S solution several times. The residue consists of the sulphides of Cu, Pb, Fe and Zn, while the filtrate contains Sn and Sb also As if present (Method of A. Rössing).¹

Dissolve the residue in HNO₃ and run down with H₂SO₄ for the lead. The Cu, Fe and Zn are determined as usual, the copper preferably by A. H. Low's iodometric method.² Add to the filtrate a small excess of HCl and allow to settle on the steam bath about an hour. Filter the precipitate, washing well with luke warm water to remove all H₂S. Place the paper containing the sulphides in an Erlenmeyer flask. Add a measured excess of N/10 iodine solu-

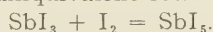
¹ Journal Society Chemical Industry, 1902, 191.
² Technical Methods of Ore Analysis.

tion, 30-50 cc. conc. HCl, and about two grams of tartaric acid. Never omit the tartaric acid, which serves to hold the antimony in solution. Insert a rubber stopper having a small swan-neck thistle tube in it to condense and retain any iodine vapors that might be evolved in heating. Heat the flask almost to boiling for a few minutes, whereupon the sulphides are changed to iodides:



As will be seen, the tin is completely oxidized, whereas the antimony goes only to the triiodide form. Cool the flask, wash out the bulb tube and dilute somewhat. Titrate the excess of iodine with a tenth-normal solution of sodium thiosulphate, using a starch indicator.

Now wash, or filter (if a sharper end point is desired), into a beaker, neutralize with Na_2CO_3 and add an excess of powdered sodium bicarbonate. Now titrate with a tenth-normal solution of iodine (Mohr's method). In this alkaline solution the antimony triiodide is oxidized to the quinivalent condition:



From this last titration the amount of antimony present can be calculated. Multiply the volume of iodine solution used in this titration by $3/2$ and subtract this from the volume of iodine consumed in the first titration. This will give the volume of iodine consumed by the tin alone.

1 cc. 0.1 N iodine = 0.006 g. Sb. $\text{SbI}_3 + \text{I}_2 = \text{SbI}_5.$

1 cc. 0.1 N iodine = 0.00298 g. Sn. $\text{SnS}_2 + \text{I}_4 = \text{SnI}_4 + 2\text{S}.$

This method of getting the tin and antimony by the titration of the sulphides is, as far as I know, original and for it I can claim several advantages. One is that the antimony is put in just the stage of oxidation that is required for Mohr's titration. Another is that it does not matter in what condition of valency the sulphides are, even free sulphur does not interfere. This fact was ascertained by taking two samples of tin of 0.1 gram each, dissolving one in conc. HCl, forming SnCl_2 , and the other in $\text{HCl} + \text{HNO}_3$, forming SnCl_4 . Analyzing as above, gave almost identical results.

The separation of the insoluble sulphides from the tin and antimony can be made almost absolute by dissolving these sulphides of Cu, Pb, Fe and Zn in hot HCl and reprecipitating by means of NaOH and Na_2S . In this manner any traces of Sb or Sn that may have been retained by the first precipitate are removed and added to the main filtrate.

To test the above method of titrating the sulphides by means of iodine, I have weighed out samples of pure tin and run them through with this method and have obtained the following close results, using the theoretical tin factor for the iodine:

Tin taken. Gram.	Tin obtained. Gram.
0.0664	0.0669
0.0702	0.0705
0.0923	0.0922
0.1132	0.1135

To further test the method, known amounts of pure copper, lead, tin and antimony were dissolved together and tested in the above manner with the following result:

	Taken. Gram.	Obtained. Gram.
Copper.....	0.2995	0.2996
Lead.....	0.2990	0.2997
Tin.....	0.0946	0.0953
Antimony.....	0.0942	0.0936

THE VOLUMETRIC CHROMATE DETERMINATION OF LEAD

By JOHN WADDELL.

Received July 10, 1911

In the Transactions of the American Institute of Mining Engineers, Vol. 35, page 359 (1905), Mr. H. A. Guess gives a method for determining lead in ores. Though it can be used for nearly all kinds of ores it is most satisfactory in just those cases for which the results obtained by the molybdate method are least reliable, namely, with ores poor in lead and containing a large amount of calcium carbonate.

Guess claims that the method is easily carried out and I understand that it is employed at the Trail Smelter in British Columbia.

It does not seem, however, to have become at all general. I have not found it in any of the books on quantitative analysis nor have I seen it described in any of the chemical periodicals. Guess describes the method as follows:

"To the ore charge of from 1 to 5 grams in a 25 cc. flask add from 3 to 5 cc. of strong nitric acid and 15 cc. of strong hydrochloric acid; digest until everything is in solution and the excess of acid has been reduced to about 8 cc. The whole operation on the hot plate requires but 15 minutes. The flask is then removed, and slightly diluted ammonia is added slowly in slight excess, the neutralizing action being sufficiently vigorous to render the contents of the flask quite hot. Acetic acid of 80 per cent. strength is then added slowly, the flask being shaken vigorously until the smell indicates a decided excess of acetic acid. Then 5 cc. of strong ammonium acetate are added to insure the solution of any lead compounds remaining undissolved by the ammonium acetate already formed in the flask.

If the ore contains no antimony or separated gelatinous silica and if the siliceous residue in the bottom of the flask is only in slight amount (as is usual with heavy lime ores or with concentrates) add to the hot undiluted and unfiltered solution an excess—about 10 cc.—of a ten per cent. potassium chromate solution. Under these conditions the bulk of the contents of the flask will not exceed 50 cc., and after shaking and letting the precipitated lead chromate settle for about five minutes the contents are filtered through an 11 cm. filter of any fairly rapid and close paper. If these directions are carried out the lead chromate will be quite granular and will show no tendency to run through. The precipitate in the flask and on the filter is washed several times with hot water containing about 0.5 per cent. of acetic acid until free from soluble chromates. The funnel

with the filter is then set over the original flask and hot, dilute hydrochloric acid (1:1) poured through the filter, dissolving the lead chromate. Further additions of hydrochloric acid are made if necessary and all lead chromate is dissolved from the filter; then it is washed with warm water until free from chromate.

The original flask now contains nothing but the hydrochloric acid solution of the lead chromate and the washings which, after adding a small crystal from 0.5 to 2 grams in weight of potassium iodide, is titrated direct with standard "hypo" solution whose value is known in terms of lead, the most suitable strength being that in which 1 cc. is equal to 5 mg. of lead. In this operation, by using only a small quantity of potassium iodide and having the solution fairly strong with hydrochloric acid (about 50 cc. of hydrochloric acid 1:1 in a total of 200 cc. of solution) and somewhat warm, any tendency of the lead to form yellow scales of lead iodide and thus somewhat obscure the end reaction with starch is completely checked and the end reaction is sharp.

The sharpness of the end point with starch, as opposed to the indistinctness of the end point in the molybdate method, is given as one of the special features.

Students working in my own and other laboratories have found difficulties with this method. Sometimes the blue color of the starch disappeared on addition of thiosulphate, only to come back in a minute or two; in other cases the precipitate of lead chromate seemed not to be washed free from soluble chromate in the course of an hour or more; sometimes even when no error was visible the results were not concordant. Owing to the difficulties experienced by my students last winter, I ran through a couple of determinations of an ore myself and obtained 23.61 per cent. and 24.10 per cent., a difference of half a per cent.

Since the method is especially interesting from an instructional point of view, I decided to investigate the points of difficulty. I may say incidentally that treatment of the ore with hydrochloric acid before the addition of nitric acid is to be recommended, since it lessens the tendency to form a globule of sulphur which may enclose some lead.

The effect of varying the strength of acid used in the titration was first tried. To about 10 cc. of a solution of chromate (9.4 grams per liter) 200 cc. of a mixture of strong hydrochloric acid and water in which the acid varied between 5 cc. and 100 cc. were added, and after addition of potassium iodide the iodine was titrated with thiosulphate. With small quantities of acid the blue color of the starch, after being first discharged, came back after a minute or two. With 5 cc. of acid the color was discharged and reproduced several times, and even with 20 cc. the color came back once. It seems that there should be at least 25 cc. of acid present.

Titration in which the chromate had been heated with acid for varying lengths of time between 60° and 80° C. showed in general partial decomposition,

though the variations were not always of the order that might be expected.

As there is evidently a time reaction between the chromate, hydrochloric acid and potassium iodide, the effect of varying amounts of iodide, up to 1 gram, were tested. The most concordant results were obtained by using one gram of iodide, and by running in the thiosulphate drop by drop, about three drops a second, 1 cc. of chromate in that case being equal to 1.968 cc. and 1.976 cc. of thiosulphate in duplicates. In this set of experiments 25 cc. of acid and 175 cc. of water were added to 15 cc. of a chromate solution measured by a pipette.

One source of error in the method was found to be the solubility of lead chromate in the 0.5 per cent. acetic acid used for washing. The addition to 50 cc. of this acid of two or three drops of a solution containing less than one per cent. of chromate rendered its solvent action almost nil, and hence the acid may be used till nearly all the soluble chromate is washed out, but finally pure water is required.

In order to avoid possible error from setting free chlorine by the use of half and half hot hydrochloric acid, I dissolved the lead chromate with a cold mixture of 25 cc. of hydrochloric acid and 75 cc. of water, washing alternately with this mixture and with cold water. From time to time 5-10 cc. of hot water were used for the more perfect dissolution of the lead chloride.

The precipitate having been all dissolved and washed into the flask as Guess describes, the liquid was made up to about 200 cc. and one gram of potassium iodide was added, followed immediately, to avoid loss of iodine, by thiosulphate from the burette at the rate of two or three drops a second. After the brown color had nearly disappeared and had given place to a dark green, starch was added and the thiosulphate run in, a few drops at a time, with vigorous shaking. When the blue color was nearly discharged I added 10 cc. of strong hydrochloric acid and heated the flask to 40° C., after which two or three drops of thiosulphate were sufficient to bring the clear green color of the chromic salt, which constitutes the end point.

The following results were obtained, using the modified method:

Twenty-five cubic centimeters of a solution of pure lead containing 0.150 gram of lead required in duplicate determinations 30.65 and 30.51 cc. of thiosulphate. A student who made a check determination used 30.50 cc. The average is 30.55 cc.; or 1 cc. thiosulphate equals 0.00491 gram lead.

A solution of ore was made, such that 25 cc. would require somewhere about 30 cc. of thiosulphate. In four determinations, the figures obtained were 28.73, 29.25, 29.25 and 29.25 cc. A student made a check determination, dissolving the lead chromate in 50 cc. of 1:1 cold hydrochloric acid and using half a gram of chromate. He required 29.04 and 28.97 cc. of thiosulphate.

Afterwards I made four determinations, taking half a gram of ore and required 28.30, 28.40, 28.28

and 28.30 cc. of thiosulphate. The lowest and highest figures give respectively 27.76 and 27.88 per cent. of lead.

The difference between the Guess method of solution of lead chromate and the one which I adopted was tested by sprinkling basic lead chromate upon two filters and dissolving one quantity with nearly boiling 1 : 1 acid and the other in the manner I have described. In the first case 1 cc. thiosulphate = 0.01516 gram chromate; in the second 1 cc. thiosulphate = 0.01446 gram chromate.

Assuming that the second determination was correct, the 0.4336 gram of chromate used in the first case should have required 29.99 cc. of thiosulphate instead of 28.60 cc., which was actually used. With starch iodide paper, chlorine can be readily detected when hot 1 : 1 hydrochloric acid is put upon lead chromate.

In the presence of large quantities of iron, say 20 per cent., the tendency to form basic acetate gives difficulty in dissolving the lead. Of course, any ferric acetate precipitated along with lead chromate is fatal. Guess points out that the presence of antimony, bismuth, silver or gelatinous silica interferes with the process, but says that if the lead is first changed to sulphate and, after separation from the soluble sulphates, dissolved in ammonium acetate as for the molybdate determination, the rest of the process may be carried out as before. In this case the only advantage in the chromate method is its delicacy; it takes a longer time, but duplicate determinations should check within a tenth of one per cent., and often do check within two or three hundredths.

I wish to acknowledge help given by several students, particularly by Mr. H. Bradley and Mr. W. Agassiz.

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NOTES ON THE DETERMINATION OF ACIDS IN SUGAR CANE JUICE.

By P. A. YODER.

Received May 22, 1911.¹

In a previous report² reference was made to an investigation of the acid constituents in sugar cane juice and its products, which I commenced at the Louisiana Sugar Experiment Station, and I mentioned some of the analytical difficulties encountered in determining certain of these constituents, reporting in detail the development and application of a polariscopic method for the determination of malic acid (and incidentally also of tartaric acid). While work upon the general problem of the acid constituents was interrupted before it was sufficiently rounded off to admit of a report being made on the subject as a whole, yet, besides the work on malic acid already reported, there are other results among those thus far obtained, both on analytical methods and in the

examination of cane products, which I deem should be made available to others who may be working on the same or on similar problems. I shall present, therefore, in the following some notes on analytical operations and some determinations and approximate estimations of acid constituents in the cane juice without presuming in this to report a satisfactory scheme of analysis or the results of ultimate determinations of all the acids present.

In the early stages of the work, after finding that usual methods of determining and identifying commonly occurring organic acids not to work satisfactorily, a number of other methods described in text books and the periodical literature and modifications and combinations of these methods were tried. In these preliminary tests of methods, I was assisted by Mr. W. G. Taggart, assistant chemist, who, under my direction, applied them variously—to cane juice, to solutions of molasses or molasses and sugar, to such solutions with added known amounts of certain acids, to solution of definite quantities of sucrose, dextrose, and levulose with or without additions of the acids in question, and to solutions of one or more of the acids alone in water.³

With the exception of a method of Behr⁴ for the separation of the aconitic acid as its acid ammonium salt, practically all the methods described in the literature which we tried were worked out by the authors primarily for the analysis of wines and other fermentation products and fruit juices, and none of them take into consideration the possible presence

¹ Among the methods receiving special consideration in our experiments are the following:

1. The method of G. Jörgensen (*Z. Unters. Nahr.-Genussm.*, **13**, 2-257 (1907); *Chem. Abstr.*, **1**, 1448-52 (1907)), for tartaric, succinic, citric and malic acids, in which, after separating the acids from some of the other matters by means of the lead salt, the tartaric acid is separated as the acid potassium tartrate, the succinic then shaken out with ether and subsequently the citric and the malic acids converted to the barium salts and their separation effected by a procedure based on a difference in the solubility in 50 per cent. alcohol.
2. The method of R. Kunz (*Z. Unters. Nahr.-Genussm.*, **6**, 721 (1900); **12**, 641-5 (1906); *Chem. Zentr.*, **II**, 854 (1903); **I**, 418 (1907)), for the succinic acid, involving the extraction with ether by an extraction apparatus according to Schacherl, and the subsequent oxidation by potassium permanganate of other acids than succinic.
3. The method of Möslinger (*Z. Unters. Nahr.-Genussm.*, **4**, 1120 (1901); *Chem. Zentr.*, **I**, 231 (1902); **II**, 1386 (1903)), for lactic acid, in which its separation from malic and tartaric acids is based upon the solubility of its barium salt in 75 per cent. alcohol.
4. The method of C. Schmidt and C. Heipe (*Z. anal. Chem.*, **21**, 1 (1882)), for tartaric, succinic, and malic acids, making use of the calcium salts to separate the tartaric acid from the others, and of the barium salts to separate the succinic from the malic acids. Also a modification of this method ("Official and Provisional Methods of Analysis," U. S. Dept. of Agriculture, Bureau of Chemistry, *Bull.* **107** (revised), p. 80) in which succinic acid is disregarded and citric acid is separated from the malic acid by heating the water solution of the calcium salts of the two.
5. The method of F. Mutel (*Annales des Falsifications*, **2**, 383 (1882)), for tartaric, citric and malic acids, in which the tartaric acid is separated as the acid potassium salt and the other two are separated from each other as the barium salts, by a half volume of alcohol.
6. The method for tartaric acid by J. von Ferentzy (*Chem. Ztg.*, **1**, 1118 (1907)), as applied by L. Gowing-Scopes (*Analyst*, **33**, 315-9 (1908)), in which the tartaric acid is precipitated as a basic salt by the magnesium mixture and thus separated from the malic or succinic acids.
7. The method for separating aconitic acid by A. Behr (*Ber. chem. Ges.*, **10**, 351 (1877)), in which the acids are first separated in a definite state by means of the lead salts and hydrogen sulphide, then the acid ammonium aconitate formed, which proved to be a suitable compound for further purification, liberating the acid finally with sulphuric acid and shaking out with ether.

² *Loc. cit.*

¹ This paper is an abridgement of a paper by the author on the same subject presented at the 42nd General Meeting of the American Chemical Society, July 12, 1910.

² *This Journal*, **3**, 563-574 (1911).

aconitic acid. The aconitic acid, however, has been found present in cane juice and its products by Behr,¹ in sugar beet products by v. Lippmann,² and in sorghum by Parsons.³ My own investigations, as will be shown further on, proved this acid to be not only present in Louisiana cane juice and molasses, but to be the predominating one of the acids. As aconitic acid and its salts are, in most of their properties which are involved in the analytical operations, very similar to some of the other acids commonly occurring in plant juices, its presence in the cane products especially complicates the problem of determining which of the other acids are present and in what quantities. The methods available, even in the absence of aconitic acid, are sadly deficient as means of sharp-cut separations. These circumstances led me to make many preliminary experiments on the properties of some of the salts, and the behavior of the acids under various possible treatments for their separation. The results from some of these lines of preliminary experiments are submitted in the following:

I. SOME RESULTS FROM PRELIMINARY TESTS.

1. *Extractibility of the Free Acids with Ether.*—In the method of Jörgensen⁴ in its original form, which method first of all I attempted to apply, we are directed to shake out with ether, repeating two or three times. This proved to be insufficient to extract even 90 per cent. of the succinic acid, as may also be calculated from theoretical grounds, basing the calculations on the relative solubilities of the acid in water and ether. By trial with a solution of succinic acid, making three extractions with equal volumes of ether each time, we recovered less than half the acid. More recently Jörgensen has published a modification of his method⁴ in which he requires more thorough extraction. As aconitic acid is also readily extracted with ether, it is evident that with the cane products it would not suffice simply to titrate this extract with a standard alkali to determine the succinic acid in it. Kunz⁵ offers a procedure with the ether extract to get the true amount of succinic acid, involving the oxidation of the acids other than succinic acid with potassium permanganate in an acid solution, then precipitating the succinic acid with standard silver nitrate solution and titrating back the excess of silver nitrate. He also suggests a more satisfactory way of extracting the solution with ether, using a form of what some German writers⁶ have chosen to call "perforation apparatus." Kunz used the Schacherl⁶ apparatus. Not having this apparatus on hand, I improvised a substitute which was more efficient and at the same time very simple in construction, using it on an ordinary ether extraction flask, and with a tin spiral condenser (see Fig. 1). The tube *B* to hold the liquid to be extracted may

be chosen of a size to suit the volume, increasing also the size of the outside tube *A*, if necessary. Tube *A* has three indentations around the conical part at the bottom to prevent tube *B* from sealing off the communication with the ether flask below. To avoid too rapid a delivery of ether while filling or under irregular returning from the condenser, so as to cause some of the water solution to be carried over, the openings

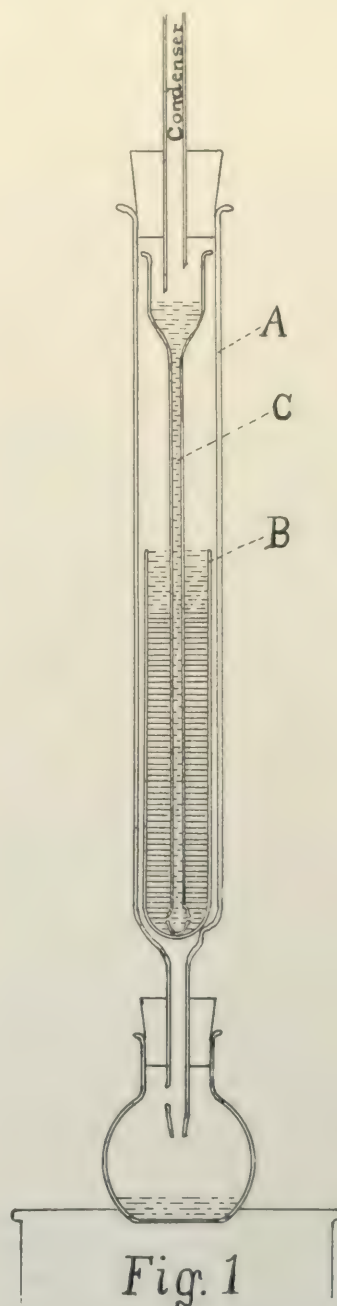


Fig. 2

at the bottom of the delivery tube *C* should be suitably constricted. Evidently a similar apparatus could be used for extraction (or "perforation") with a heavier liquid like chloroform. For *B* we could substitute one like that represented in Fig. 2 and tube *C* can be omitted or else shortened and suspended with its lower end at the surface of the liquid in *B*. The

¹ Loc. cit.

² Ber. d. chem. Ges., **12**, 1649 (1879).

³ Am. Chem. J., **4**, 39; Ber. d. chem. Ges., **15**, 1763 (1882).

⁴ Z. Unters. Nahr.-Genussm., **17**, 396 (1909). Chem. Abstr., **3**, 1781 (1909).

⁵ C. v. d. Heide and H. Steiner, Z. Unters. Nahr.-Genussm., **4**, 114-6 (1902).

⁶ Ibid., **4**, 174-6 (1902).

solutions with which I had occasion to deal showed little or no tendency to emulsify, therefore I could hurry the extraction as much as the efficiency of my condenser allowed. A tin spiral condenser with an inside diameter of only $\frac{1}{4}$ inch proved too small for the return flow during rapid boiling, yet even with such and with the cooling water at 20 to 23°, 10 hours sufficed to extract practically all the succinic acid. With $\frac{3}{8}$ -inch tin tubes for condensers to this apparatus, the time could doubtless be reduced to 5 or 6 hours. C. v. d. Heide and H. Steiner¹ have recently subjected the Kunz method for determining the succinic acid to a critical study, and the former of these describes a more complicated apparatus which should be more efficient provided the condenser has sufficient capacity. They report 9 hours, when boiling as fast as they did, usually required for complete extraction, recommending 12 hours for certainty in all cases. They also conclude that the oxidation of other substances accompanying the succinic acid should be carried out in the neutral solution instead of the acid solution.

A number of extraction tests were made with other organic acids under similar conditions to determine approximately to what extent these would accompany succinic acid, to disturb the acidimetric titration of the extract as a measure of the succinic acid, or to occasion losses in the water solution if that is to be used for the determination of other acids, *e. g.*, citric and malic.

Aconitic acid in tests made with solutions of the acids derived from cane juice seemed to be extracted about as rapidly as succinic acid from solutions to which the latter had been added.

In tests with 0.1 *N* citric, tartaric, or malic acids, the same rate and time of boiling which would completely extract the succinic acid, sufficed to extract 37, 23 and 53 per cent., respectively, of these acids, and with mixtures of any two of these approximately the same proportions of those present were extracted, as when each was present alone. In mixtures containing malic and tartaric acids, the amount of each was determined by the polariscopic method reported in a previous paper.² With lactic acid, about twice the time required for succinic acid sufficed for complete extraction of the lactic acid. The extract, after dissolving in water, had practically the same proportion of lactic to actual lactic acid as the original solution, as may be expected from equilibrium considerations.

From the foregoing it is evident that the succinic, aconitic, and lactic acids can readily be extracted quantitatively with ether by use of a suitable apparatus, but that it is hardly practicable to extract tartaric, citric, or malic acids quantitatively from their solutions in water. The tests show, also, that the first three acids, if extracted from a solution containing also one or more of the last three, will not thereby be separated free of the last three, and that the residual water solution will not contain the total

of the last three. The separation may, of course, be accomplished more nearly quantitatively by redissolving the ether extract in water and reextracting, and repeating this as often as necessary to attain the degree of accuracy desired.

2. *Solubility or Precipitability of the Acids as Calcium Salts.*—In the first series of tests under this heading, the salts were formed by the addition of calcium acetate in excess to solutions of the free acids. In these, of course, acetic acid is a by-product. In later tests with a few of the acids, the salts were formed by the addition of milk of lime and lime water to the acid, in some cases just to neutralize and in others in excess. In the first series only broad approximations were aimed at, no very definite conditions as to temperature, agitation, and time of standing being maintained. The results from either series have no value as accurate physical constants, but can serve the purpose of suggesting methods for the separation of the acids, allowing, of course, also for the possible modifying influence of other substances present in natural products upon the solubility of these salts. The tests were made by trying different concentrations until a strength of the acid was reached which would just suffice to call forth a precipitate with the excess of calcium acetate, or calcium acetate and 95 per cent. alcohol sufficient to make 50 per cent. alcohol or 85 per cent. alcohol. Unless otherwise stated, the results given in the accompanying table represent upper limits in strength (in grams per 100 cc. before the addition of alcohol) which would not suffice to give precipitates immediately or very soon, and without rubbing the sides of the tube or inoculating with crystals of the same salts.¹

TABLE I.—UPPER LIMITS, IN GRAMS ACID IN 100 CC. WATER WITH EXCESS OF CALCIUM ACETATE, WHICH DOES NOT CAUSE A PRECIPITATE.

Acids used.	In water alone.	With addition of alcohol to 50 per cent.	With addition of alcohol to 85 per cent.
Tartaric acid	Less than 0.1 if stirred for some time	0.13 for immediate precipitation	0.01
Citric acid	More than 0.32 if cold Less than 0.32 if hot	0.08	0.005
Aconitic acid	More than 5.00 cold or hot ²		
Malic acid	More than 5.00	0.14, less if heated 0.88	0.005 0.03
Succinic acid	More than 5.00	2.5, but after starting much ppt. formed	0.05

Calcium acetate alone in water solution, if too concentrated, will gelatinize or form a jelly-like precipitate on addition of alcohol. Between 5 and 6² per cent. was found to be the upper limit in concentration of the water solution which will not give a precipitate when 95 per cent. alcohol is added until an alcoholic concentration of 85 volume per cent. is reached.

In a series of tests in which the calcium salts of citric, aconitic, and malic acids were formed by the addition of calcium hydroxide to the free acid, and

¹ The supply of alcohol from which I used was later discovered to have a considerable acidity, due to volatile acids, which may have exerted some influence in keeping more of the salts in solution.

² See, however, the discussion of aconitic acid below for the behavior of its calcium salt in a neutral solution when heated.

¹ Z. Unters. Nahr.-Genussm., 17, 291-307, 315-320 (1909).

² THIS JOURNAL, 3, 563-574 (1911).

in which the alcohol used was absolute alcohol, results were obtained differing in some particulars from those given above, and showing also, in the cases tried, a marked difference in the solubility of the salt in a solution exactly neutral (to phenolphthalein) and one having an excess of calcium hydroxide.

With tartaric acid: The concentration in a neutral water solution which, without addition of alcohol, fails to give a precipitate within 20 hours, lies between 0.025 and 0.05 per cent. With the addition of an equal volume of alcohol, the limit is between 0.025 and 0.033 per cent. for immediate precipitation and between 0.0033 and 0.0045 per cent. for precipitation on standing 20 hours. The mother liquor, from which calcium tartrate was precipitated by addition of an equal volume of alcohol and standing 20 hours, contained in two trials the equivalent of 0.0021 per cent. and 0.0030 per cent., respectively, of tartaric acid, computed on the volume of water exclusive of the alcohol.

With citric acid: The limit in water solution with calcium hydroxide to exact neutrality was about 1.42 per cent. in the cold and between 0.25 and 0.3 per cent. in the boiling hot solution, and in each case it was less with an excess of calcium hydroxide.

With aconitic acid: A 10 per cent. solution of the acid in water, neutralized with dry calcium hydroxide, was insufficient to give a precipitate in the cold. Heated to boiling, a 1 per cent. solution, calculated as free acid, sufficed to call forth a precipitate of the calcium salt. In other experiments it developed that the water adhering to the precipitate of (impure) calcium aconitate, on decanting from the precipitate formed on boiling, sufficed to dissolve the precipitate on cooling.

With malic acid: 0.25 per cent. of the acid, exactly neutralized with calcium hydroxide, just sufficed to bring forth a precipitate upon addition of an equal volume of absolute alcohol. With an excess of calcium hydroxide, considerably less sufficed.

With lactic acid: A 10 per cent. solution, neutralized with calcium hydroxide, did not give a precipitate, even when an equal volume or when 8 volumes of absolute alcohol were added.

From the foregoing notes on aconitic acid, we can correct the impression that is current and is frequently reproduced in text-books,¹ that the citric acid is the only one of the natural organic plant acids whose calcium salt is less soluble in hot than in cold water. The difference between the solubility of the calcium salt in cold and in hot water is in fact greater in the case of the aconitic acid than in the case of the citric acid.

With lactic acid: A solution of the acid, neu-

tralized with calcium hydroxide and made up to a 15 per cent. solution, gave no precipitate when an equal volume of 95 per cent. alcohol nor any immediate precipitate when 14 volumes of 95 per cent. alcohol were added.

The solubility of the malate of lime in 50 per cent. alcohol is so much greater than that of the lime salts of the other acids mentioned, excepting lactic acid, and so much less soluble in 85 or 90 per cent. alcohol than the calcium lactate, that this affords us a means of removing from malic acid the main bulk of these other acids, if present in sufficient quantity to interfere with my polariscopic method for estimating malic acid, as suggested in my report on that method.²

3. *Solubility or Precipitability of the Acids as Barium Salts.*—The properties of the barium salts of these acids are in many respects known to be analogous to those of the calcium salts. With lactic acid direct tests were made on the solubility of the barium salt with results same as noted above for the calcium lactate. In the application to the acids of cane juice of a method of separation by means of the barium salts, depending upon their different solubilities in water and in alcoholic mixtures of different strength, as in Jörgensen's³ method above referred to, the aconitic acid, if present, may be precipitated partly with citric acid and partly with malic acid. Thus in an attempted determination of the cane juice acids by Jörgensen's method, before this fact was taken into consideration, we obtained results indicating from 0 to 0.033 per cent. citric acid and from 0.059 to 0.094 per cent. malic acid from the same sample, according to the number of times we would redissolve and reprecipitate, when in fact, as afterward proved, the sample had but traces or none of these two acids present.

4. *The Acid Ammonium Salts of Aconitic, Citric, and Succinic Acids.*—Behr⁴ made use of an acid ammonium salt for the purification of aconitic acid, forming it by saturating a portion of the aconitic acid with ammonia, boiling to drive off the excess of ammonia, then adding an equal amount of the free acid. In my work on cane juice acids this method also served this purpose admirably. However, in parallel tests with solutions of succinic acid (which, if present, might accompany aconitic acid in an ether extract) the results were so nearly analogous that this acid ammonium salt could hardly serve as a means for the quantitative separation of these two.

5. *Von Stahre's⁵ Pentabrom Acetone Reaction and Denige's⁶ Acetone Dicarboxylic Acid Reaction as Means of Detecting and Identifying Citric Acid.*—The former of these reactions did not, in our hands, prove a very delicate test for citric acid. The latter reaction, however, is very delicate. Denige's reagent is 5 g. mercuric oxide in 20 cc. concentrated sulphuric acid and 100 cc. water. To 4–5 cc. of the solution (which

¹ Fresenius, "Anleitung zur qualitativen chemischen Analyse," 16th Ed., p. 437; Allen, "Commercial Organic Analysis," 3rd Ed., Vol. I, p. 530. (Into the latter treatise has crept the misleading statement: "Aconitate of calcium, $\text{Ca}_3(\text{C}_6\text{H}_3\text{O}_6)_2 + \text{H}_2\text{O}$, forms small crystals which require 100 parts of cold water for solution, but are much more soluble in boiling water. Hence aconitic acid gives no precipitate with lime water either in the cold or on boiling, a behavior which distinguishes it from citric acid." The latter statement may be true for so dilute a solution as lime water, but could not be said to apply to a much stronger solution, such as might be obtained by adding milk of lime to aconitic acid.)

² THIS JOURNAL, 3, 563–574 (1911).

³ Z. Unters. Nahr. Genussm., 13, 241–257 (1907); Chem. Abstr., 1, 1448–52 (1907).

⁴ Ber. d. chem. Ges., 10, 351 (1877).

⁵ Chem. Zentr., 11, 418 (1895).

⁶ J. Soc. Chem. Ind., 1898, 802; Chem. Zentr., 11, 134 (1898).

should be very dilute in citric acid) is added 1 cc. of Denige's reagent and heated to boiling, then 5 to 6 drops of a 2 per cent. potassium permanganate solution are added. With citric acid in quantities down to mere traces, the first drop of potassium permanganate solution would always call forth a cloudiness due to a very finely divided, readily subsiding precipitate. The test was tried upon the following other substances: aspartic, malic, oxalic, tartaric, lactic, glycolic, fumaric, and succinic acids, and upon pure sucrose. None of these gave a reaction likely to be mistaken for that from citric acid. Oxalic acid gave a white precipitate with the mercury reagent alone, but when this was filtered off, and the potassium permanganate added to the filtrate, no additional precipitate was formed. The test revealed citric acid also in the presence of any of these substances.

When, however, the test was applied to a sample of aconitic acid, which we had on hand, it gave apparently the same reaction as citric acid, differing only in that it was usually not until the second or third drop of potassium permanganate solution was added that the fine pulverulent precipitate formed. Another preparation of aconitic acid, supplied by Messrs. Eimer and Amend, likewise gave the reaction. Whether this was due to contaminations with citric acid, from which the aconitic acid was presumably prepared, remains undetermined. Considering, however, the close relation in constitution, of the aconitic to the citric acid, on the one hand, and to the acetone dicarboxylic acid on the other, I think there is but little doubt that the aconitic acid itself is capable of giving this reaction. We may likewise expect the tricarballic acid to give this reaction. Since aconitic acid and possibly also tricarballic acid are present in the cane juice, the fact that we got the reaction in cane juice with Denige's reagent does not prove either the presence or the absence of citric acid. The fact that here also not the first drop of potassium permanganate called forth the precipitate is some evidence that it is not present.

II. EXAMINATION OF SAMPLES OF CANE JUICE.

From the many samples of juice, molasses, and unrefined sugars examined by one or another course of procedure, I shall here report merely a few of the more definite or conclusive findings from one of the samples, with a few references to results from other samples for comparison.

The sample consisted of 6 liters of juice pressed from cane harvested at the beginning of the season, about Oct. 1, a mixture of the four varieties, D74, D95, La. Purple, and La. Striped.

The initial operations were as follows: The juice was neutralized with sodium hydroxide, precipitated with neutral lead acetate and an equal volume of 95 per cent. alcohol, filtered next day and the precipitate washed with 50 per cent. alcohol, then suspended in hot water, decomposed with hydrogen sulphide, filtered, and the filtrate concentrated upon the water-bath to a small volume. A small portion of this was titrated with normal potassium hydroxide. It indicated acidity in the total residue equivalent to 125.1

cc. normal acid. The titrated portion was united with the rest, the whole diluted with water and precipitated with an excess of calcium acetate and alcohol to an alcohol concentration of 85 per cent. After standing a day it was filtered. The precipitate of calcium salts was treated three times with water, twice with 200 cc. and once with 50 cc. The water solutions were each treated first with alcohol to 50 per cent., filtering after one or more days, then the filtrates further treated with alcohol to 85 per cent., filtering after one or more days. The insoluble residue (which I shall designate A), the precipitates from 50 per cent. alcohol (B, B', and B''), and those from 85 per cent. alcohol (C, C', and C'') were each investigated further by a different course of procedure. Many different operations were applied to these residues and products from them, some of which will be mentioned in the following paragraphs in connection with individual acids reported upon.

1. *Oxalic Acid*.—This acid, if present, should have been in the residue A, of calcium salts which failed to dissolve in water. This residue was treated with acetic acid; the portion not dissolved in acetic acid was dissolved in hydrochloric acid, then reprecipitated with ammonium hydroxide and calcium acetate, acidifying again with acetic acid. A small precipitate was hereby obtained, equivalent to 0.0027 gram oxalic acid. With manganese dioxide and sulphuric acid this residue evolved carbon dioxide, thus verifying the conclusion that it is an oxalate.

2. *Phosphoric Acid*.—This made its appearance in three different residues, two of them from residue A above, which had failed to dissolve in water, and one from a combination of B and B' precipitates from 50 per cent. alcohol. Residue A was treated with acetic acid, the solution in acetic acid was treated with alcohol to 50 per cent., and both precipitate and filtrate examined for phosphoric acid. The precipitate had 0.1586 gram, computed as P_2O_5 . The acidified alcoholic filtrate, after conversion by means of potassium carbonate to the potassium salts and examining for tartaric acid, proved to contain 0.0241 gram phosphoric acid as P_2O_5 . From the residue B and B', obtained by dissolving in water and reprecipitating from 50 per cent. alcohol, I separated 0.0060 gram as P_2O_5 . Thus a total of 0.1887 g. phosphoric acid as P_2O_5 was found.

3. *Sulphuric Acid*.—No effort was made to trace this out quantitatively in all the residues in which it might occur, viz., A, B, B' and B''. In a product from C', the precipitate from 85 per cent. alcohol, I also found a trace of sulphuric acid. From residues B and B', after further operations that might have occasioned small losses, I found 0.0305 g. sulphuric acid as SO_3 .

4. *Tartaric Acid*.—The calcium tartrate, if present in large quantity, should have appeared in A; or if present in small quantity, it should have appeared only in residues B, B', and B'', or possibly in small traces in residues C, C', and C''. Products from A, B, and B', tested in small volume for tartaric acid by conversion to the acid potassium salt, gave nega-

tive results, hence tartaric acid cannot be present in more than mere traces. In other more direct tests made upon cane syrup it also proved to be absent there, in that the acids from 100 grams syrup, separated by use of the lead salts, gave no precipitate from 50 cc. solution in water after neutralizing with calcium hydroxide. This was further verified by the polariscopic method with the uranium compound, in that the uranium produced little or no change in the optical activity.

5. *Malic Acid*.—This, if present, should have appeared in residues C, C', and C'', precipitated from the 85 per cent. alcohol, but principally in C. From this residue the acids were set free by converting them into the lead salts and decomposing the lead salts with hydrogen sulphide as in the initial operations with this sample of juice. The acids thus liberated were examined by the polariscopic method with the uranium salt¹ and showed a mere trace of malic acid present, *viz.*, 0.0170 gram. C' and C'' similarly yielded 0.0101 and 0.0040 gram, respectively. From B and B' combined, there were recovered additional traces, 0.0095 and 0.0054 gram. The total in these five portions is 0.0461 gram. Tests with cane syrup, as stated in the former report, gave results indicating about 0.01 to 0.03 per cent. malic acid in the syrup.

6. *Succinic Acid*.—This should be found principally in residue B, B' and B''. B and B', combined and dissolved in water, was divided into two portions. The first portion of $\frac{1}{3}$ was acidified and extracted with ether by use of the apparatus previously described. In the first five hours, with slow boiling, 0.7438 gram was extracted; in the next 15 hours, 0.1489; and in the next 12 hours, 0.0212 gram. Each residue was dissolved in 25 cc. ether and $\frac{1}{3}$ of each taken. These portions were combined, the ether evaporated, the residues dissolved in water, acidified with sulphuric acid, oxidized with an excess of potassium permanganate, again extracted, the extract residue neutralized and tested with silver nitrate according to Kunz.² It gave no precipitate, hence there was no succinic acid present. The other $\frac{2}{3}$ of the above extracts, after first separating the main bulk of the aconitic acid by heating the solution of the calcium salts, was also tested by Kunz's method for succinic acid and none found.

7. *Aconitic Acid*.—This acid should be mainly in residues B, B', and B'' with smaller amounts also in C, C', and C''. Being readily soluble in ether when free, it should appear along with succinic acid, if the latter were present, in the ether extracts. By conversion of a portion of these residues into the acid-ammonium salt, the crystallization took place so readily and so completely as to make it evident that it was almost pure aconitic acid. The first crystals of brownish color were recrystallized several times from 50 per cent. alcohol to purify a portion, then, when quite colorless, were decomposed with sulphuric acid, extracted with ether, and a melting point determination made. The purified specimen melted at

183–184°, commencing to decompose at the same time. Because of incipient decomposition, and possibly incomplete purification of so small a sample, the melting point was not very sharp, but was near enough to that found by Behr, *viz.*, 187–188°, that this taken in connection with the other properties makes the conclusion that it is aconitic acid a safe one. The first and second residues, mentioned in the preceding paragraphs on succinic acid, extracted by ether from $\frac{1}{3}$ of the solution from B and B' combined, proved on titration to have total acids equivalent to 14 cc. normal acid, which, computed as aconitic acid, amounts to 0.8123 gram (out of 0.8927 gram air-dried residue) or for the total from residues B and B', 2.437 g. No further tests were made to determine the degree of purity of the aconitic acid in these extracts than the indications furnished by the crystallization of the acid ammonium salt above referred to, nor were the smaller residues B'', C, C', and C'' further examined for aconitic acid. Each of these was, in all probability, mainly aconitic acid, except for the small traces of malic acid found in C, C', and C''. Acidimetric titrations of the several acid residues examined from malic acid showed a total acidity, not accounted for as malic acid, equivalent to 0.625 gram aconitic acid, computed upon the whole of the sample. The indications from all these crude acid residues point to about 3 grams, or 0.05 per cent., as the total of aconitic acid in the sample.

In another sample of 5 liters of juice from the same cane, the acids were similarly separated in the free state by means of the lead salts. This acid residue was subjected to ether extraction more directly than was the case in the sample above reported. The total extraction residues after the evaporation of the ether were 2.1542 grams from the first 9 hours, 0.4082 gram from the next 11 hours, and 0.0785 gram from the next 6 hours, a total of 2.6409 grams, or 0.05 per cent. These residues gave the same evidence of being almost wholly aconitic acid, when a pure specimen was prepared from them by means of the acid ammonium salt. The indication as to quantity of aconitic acid in the juice is therefore about the same in this as in the other sample.

8. *Citric Acid*.—This acid, if present, should have appeared in residues B, B', and B'', precipitated as calcium salts from 50 per cent. alcohol. Some products from B and B' which should have contained accumulations of citric acid, if present, could not be made to yield the characteristic crystals of the barium salt. From a new sample of 200 grams cane syrup the acids were separated by means of the lead salts and hydrogen sulphide as in this sample. The acids were converted to the calcium salts, and the solution treated with an equal volume of alcohol. The precipitate thus formed, dissolved in 450 cc. cold water, was heated to boiling and filtered hot. The precipitate thus separated was converted to the barium salt, but did not yield the characteristic barium citrate crystals. I conclude that the citric acid is not present in the juice nor in the syrup used in these tests.

¹ THIS JOURNAL, 3, 563–574 (1911).

² *Loc. cit.*

TABLE II.—SUMMARY OF CONCLUSIONS ON ACIDS IN CANE JUICE ANALYZED.

Names of acids.	Amount from	Gram acid per 100 cc. juice.
	the 6 liters of juice. Grams.	
Sulphuric acid (as SO_3), total not determined.....	0.0305	0.00051
Phosphoric acid (as P_2O_5).....	0.1887	0.00314
Oxalic acid.....	0.0027	0.00004
Tartaric acid.....	none	none
Malic acid.....	0.0461	0.00077
Succinic acid.....	none	none
Aconitic acid, not determined but indications of about.....	3.0	0.05
Citric acid.....	none	none
Total determined or indicated.....	3.2680	0.05447

Remarks.—If we compare the total of acids accounted for in this summary, equivalent to 60.2 cc. normal solution, with the amount of acidity found in the residue of acids after their separation from the juice by means of the lead salts and hydrogen sulphide, *viz.*, 125.1 cc. normal solution, we find that about half of the acids there present are unaccounted for. Doubtless part of this was acetic acid from lead acetate not completely washed out of the precipitate. Lactic acid was not looked for. If present it would have been left as a calcium salt in the 85 per cent. alcohol which was discarded. Nor was any account taken of tricarballic acid, which v. Lippmann¹ found in sugar beets, along with citric acid and aconitic acid. Some work started on the volatile acids was interrupted before it was finished and no report of interest can at present be made on these nor on such other acids as may be present which are not precipitated with lead acetate. It seems clear from the work thus far accomplished that aconitic acid is the predominating one among those precipitated with lead salts in a neutral 50 per cent. alcohol mixture. The only others thus far identified that are present in significant amounts are phosphoric and sulphuric acids. Oxalic, tartaric, succinic, citric, and malic acids are either completely absent or are present in such small quantities as to have no practical significance to the manufacturer. These facts may have important significance to the sugar chemist and manufacturer, who is seeking to improve the sugar house and refinery operations so as to secure more complete exhaustion of the molasses or to prevent the formation of scale in the evaporation apparatus. This relatively high percentage of aconitic acid is a special characteristic of sugar cane juice and its unpurified products. The suggestion that it occasions the peculiar cane flavor in these products, however, finds no support in the taste of the purified acid, nor in odor or taste developed in heating aconitic acid or its salts, or mixtures of these, with sugar. The free acid facilitates the browning of sugar upon heating, as do also other acids, *e. g.*, tartaric, citric or malic. The phosphoric acid is doubtless removed in part in the clarification process if the juice is limed to neutrality. Such of the phosphate and the sulphate of lime as remains in the clarified juice may become the cause of the formation of scale. With reference to the extraction of sucrose from the molasses, it would

be interesting to know what are the "molassigenic values" of the aconitic acid and its several salts, *i. e.*, their power of preventing or facilitating the crystallization of sucrose. The high solubility of the lime salt of aconitic acid, even in the hot solution, makes it improbable that any notable quantity of the aconitic acid is removed in the clarification process in which lime is used, or that it is deposited as a scale or sediment during the evaporation in the "effects" or the "pan," unless the presence of sugars to the point of saturation materially reduces the solubility of the calcium aconitate. The aconitic acid therefore accumulates in the molasses, where it is usually present in extraordinary large amounts.

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THE OCCURRENCE OF LEVAN IN SUGAR.

By W. G. TAGGART.

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Greig Smith and Thomas Steele² obtained from sucrose solutions inoculated with *Bac. levaniiformans* a new gum which they named levan, and of which they made a complete chemical study.

In conjunction with W. L. Owen, bacteriologist for the Louisiana Sugar Experiment Station, in his work on "The Bacterial Deterioration of Sugars"² it became necessary to study this same gum. The results agree with Smith and Steele in that levan hydrolyzes quantitatively into levulose according to the reaction $(\text{C}_6\text{H}_{10}\text{O}_5)_n + n(\text{H}_2\text{O}) = n(\text{C}_6\text{H}_{12}\text{O}_6)$; that its specific rotary power is about $[\alpha]_D = -40$; that it melts at 200°C .; does not reduce Fehling's solution; and is not precipitated by lead subacetate. Although Smith and Steele found the gum-forming organism to be present in nearly pure cultures and believed that the organism is responsible for the greater part of the deterioration of sugars in storage, they were unable to show by analysis that levan is formed in sugars.

Comparison of results obtained by analyses made monthly of a large number of raw sugars proved that the relation between the fall in single polarization and in sucrose (Clerget) could not be accounted for by inversion. In some cases, while the single polarization was found to decrease the sucrose (Clerget) would slightly increase. Bacteriological examination showed all of these sugars to contain large numbers of the gum-forming organism, and it may readily be seen that should levan be present in a sugar the single polarization would be decreased 0.6°v. for every 1 per cent. gum, and at the same time the sucrose (Clerget) would be increased 0.67°v. by the levan hydrolyzing to levulose during inversion.

To prove that levan was responsible for the unusual changes found to take place in these sugars, attempts were made to separate the gum from solutions of these sugars by precipitating it with alcohol made slightly alkaline with sodium hydroxide. This method, however, brought down so much of the other gummy matter that it was found impossible to separate small

¹ *Ber. d. chem. Ges.*, **11**, 707 (1878); **12**, 1649 (1879).

² *J. Soc. Chem. Ind.*, Nov. 29, 1902.

² *Louisiana Bulletin*, No. 125.

quantities of levan from such sugars, even where it had been added.

By adopting special methods, however, a separation of the levan from inoculated sugars was affected, thus bringing the deterioration process of sugars in line with that found to take place in sugar solutions. For this work inoculated Peruvian crystals were used. Two solutions of 14 per cent. sugar of 5 liters each were thoroughly sterilized, and then inoculated with yeast and allowed to ferment. When most of the sugar had fermented, the solutions were filtered and evaporated to 1 liter. The gum was precipitated from the concentrate by adding 3 liters of alcohol made alkaline with sodium hydroxide. After the gum had been dissolved and precipitated four times, a small quantity was obtained which was polarized, hydrolyzed, and the resulting levulose polarized:

	No. I.	No. II.	Control 99.8 sugar.
Polarization of gum.....	-0.35	-0.24	00.0
Polarization of hydrolyzed product	-0.72	-0.51	00.0
Theoretical polarization.....	-0.78	-0.53	00.0

Attempts have been made to find a means of avoiding the error in analysis which is caused by the presence of levan. The invertase method was tried and found unsatisfactory, and likewise the Andrlík urea method. In making the direct polarimetric reading in acid and urea solutions it was found that the rate at which the gum hydrolyzed was slower than the rate of sucrose inversion.

THE DETECTION OF SUBSTITUTION OF SPIRITS FOR AGED WHISKEY. A DISCUSSION OF THE CHEMICAL DATA PRESENTED IN THE TRIAL OF U. S. vs. NINE BARRELS OF WHISKEY.¹

By A. B. ADAMS, Chief Chemist, Internal Revenue Bureau.

Received April 24, 1911.

In this country when it is intended to age new whiskey, it is, as a rule, placed in Government Bonded Warehouses for the purpose. When it enters the warehouse it is stamped with what is called the "warehouse stamp" which bears the date of inspection and gauge. When the owner desires to withdraw the package, the tax is paid and a tax-paid stamp placed upon the stamp head, denoting the fact, stating also the time of tax payment and number of gallons content. This is called a "double stamped package."

The integrity of the stamp and the Government marks and brands is guaranteed by law, or rather, the Statutes provide a heavy fine and imprisonment for changing the contents of a package, unless the marks and brands are destroyed.

For many years it has been a common custom among certain dealers to take such a double stamped package, dispose of a portion, or all of its contents, and then refill the package with either an inferior grade of whiskey or alcohol diluted to the proper proof and artificially colored and flavored. This is a violation, as stated above, of Section 3455 R.S.

The past several years the Commissioner of Internal Revenue has claimed that the substitution of

other spirits in a double stamped package could be ascertained by chemical examination. This claim was vigorously disputed by the attorneys who represented the Wholesale Liquor Dealers' Association before the Bureau of Internal Revenue, it being claimed by them that packages of whiskey varied too much from one another in their chemical constituents to make such a comparison reliable.

At their request it was arranged that a case be tried before a jury, and from the many packages under seizure thirteen barrels were selected for trial. These had been seized on the premises of ——— Wholesale Liquor Dealers, Cincinnati.

As four of the packages were libeled later than the others they became two cases, namely, "U. S. vs. Nine Barrels of Whiskey" and "U. S. vs. Four Barrels of Whiskey."

The libel alleged that the barrels were substituted, or did contain other spirits than those tax-paid therein. The first part of the libel read as follows:

"First: That said ——— doing business under the firm name of ——— Co., did then and there receive and have in their possession with intent to defraud, the said nine distillers' original packages (barrels) of whiskey, which said packages had then and there contained distilled spirits other than the contents which were therein when such packages (barrels) were labeled, stamped, branded and marked by a duly appointed officer of the Internal Revenue."

As the thirteen barrels were owned and claimed by the same parties, for convenience sake, the cases were combined for trial and heard as one case.

The thirteen packages under seizure, according to the marks and brands, contained whiskey which had been produced by two reputable distillers at different periods, stored in the respective U. S. Bonded Warehouses for different periods, in order to properly age the whiskey.

NOTE.—It must be understood that the Government had absolutely no suspicion that the distillers had tampered with the packages. The proceedings were what are called "in rem"; that is, the suit was for the forfeiture of the packages and not a criminal action, the Government making no allegation as to who changed the contents of the barrels.

For several years the Division of Chemistry of the Bureau of Internal Revenue had been collecting analytical data on whiskey, in order to see if the chemical experts of the office were justified in deciding that a package of whiskey found on the market was not the identical whiskey indicated by the marks and brands. The method of procedure was as follows:

Upon the receipt, in the laboratory, of the sample of whiskey suspected by a Revenue officer of being other spirits than those indicated by the marks and brands on the package, orders would be sent to the Government officer at the bonded warehouse of the distillery, whose marks and brands were on the suspected package, to obtain from the bonded warehouse one or two samples as near as possible to the same date of inspection as the suspected sample.

The suspected and genuine would then be analyzed and the comparison of the different chemical constituents made. If the results were fairly close the sample was reported as genuine; if there was a marked

¹ Published by authority of the Commissioner of Internal Revenue.

discrepancy the sample was reported as containing other spirits than those tax-paid therein.

A large number of samples whose history was known were analyzed in the Bureau, a careful study made of the results, convincing the officials that a comparison could be made between packages of whiskey produced by the same distillery under approximately the same conditions of manufacture, storage and of age.

As the cases in suit were the first of their kind, and would, if decided favorably, be of great importance to the Government, it was decided to spare no expense or effort in developing unmistakably the truth or falsity of these conclusions. Instructions were therefore issued to the revenue officers, in whose districts the two distilleries were situated, to obtain a series of samples representing each year of the eight years of storage, about five for each year. To obtain the five samples as near as possible to the same date of inspection, and at least three samples of goods not more than a few days old but representing the production of different days.

The officers were told to select for the years in which the suspected samples were produced packages as near as possible to the date of inspection of the suspected samples. This was the only specific instruction to the officers as to particular packages.

This series of samples was desired for the following reasons:

The three samples of new goods to show that there was practically no difference in the analytical data between samples produced from different mashes and different dates of production when first distilled.

The five samples of each year as near as possible to the same date of inspection because such packages would, as a rule, have been stored under identically the same conditions, and, therefore, the differences due to the individual container (barrel) could be clearly shown if such existed.

The samples from each year to show the change in the different constituents, due to the length of storage.

No samples were obtained from packages but one year old as the data from these would have no real bearing on the case, all of the suspected samples having been from packages purporting to contain well matured whiskey.

The genuine and suspected samples were subjected by the same analyst, at the same time, to the following examination:

Proof determined by the regular Internal Revenue hydrometer (2° of proof representing 1 per cent. of alcohol by volume at 60° F.):

Solids.—50 cc. of whiskey were evaporated to dryness on the water bath, in platinum, dried for one hour at 100° C. and weighed.

Color.—Determination in Lovibond's tintometer using the Brewer's scale. The results were calculated to a one-half inch cell.

Acids, Etc.—The methods for the determination of acidity, ethereal salts or esters, aldehydes, furfural and higher alcohols were such as given in *Bulletin 107*, revised, Bureau of Chemistry, Department of

Agriculture, in the chapter on "Analyses of Distilled Spirits," pages 95-6-7 and 8, the Allen Marquarde method being used or the determination of the higher alcohols, results being expressed as amyl alcohol.

Color Insoluble in Water.—Color insoluble in water was determined by taking 50 cc. of the whiskey, evaporating to dryness, taking up the evaporated portion in 10 cc. of hot water, filtering, thoroughly washing the paper, bringing to the 25 cc. mark with water, adding sufficient alcohol to reach the 50 cc. mark or original volume. The color of this solution was then read in a Schreiner colorimeter against the untreated whiskey, the result being reported as the per cent. of color insoluble in water, a genuine whiskey seldom reading less than 70 per cent.

Color Soluble in Amyl Alcohol.—It was determined by shaking the original whiskey with amyl alcohol and estimating color dissolved in this menstruum. In the genuine whiskey the per cent. of color soluble in amyl alcohol seldom falls below 70 per cent. (the Marsh test using phosphoric acid in the amyl alcohol gives readings in excess of 90 per cent.; this test, however, was not used on these samples).

Qualitative Color Tests, Chloroform Test.—About 5 cc. of the whiskey were shaken with 5 cc. of chloroform, the major portion of the natural color being dissolved by the chloroform, artificial colors, such as burnt sugar or aniline dyes, appearing in the upper layers.

Amyl Alcohol Test.—About 5 cc. of the whiskey are shaken with 2 cc. of water and 3 cc. of amyl alcohol, the amyl alcohol dissolving the major portion of the natural color, artificial colors appearing in the watery or lower layer.

Paraldehyde Test.—The Amthor test as modified by Lasche, see description, page 101, of *Bulletin 107*, revised, for caramel.

On the accompanying sheets of analyses the results as obtained on the original samples are given. In parallel columns are also given these results calculated to 100 proof, in this way affording an equitable basis for comparing the chemical data on each sample regardless of its real proof.

The composition of the mash, as stated, is taken from official distillery records.

The serial number of the package is the number given each package, at the particular distillery, when it is inspected.

The date of inspection is the date when the package is gauged and entered in the warehouse; this is generally the day following the final distillation.

The age, by years and months, is the time elapsed between the date of inspection and the date of taking the sample, samples having been placed in glass (careful tests have proved that spirits do not change appreciably when kept in glass bottles securely stoppered); this is, therefore, the age in wood.

The degree of color soluble in amyl alcohol, column 23, in analytical table, is obtained by multiplying the depth of color, column 10, by the per cent. of color soluble in amyl alcohol, column 22.

DISTILLERY A.—Grams per 100 Liters.																										
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
					Solids.		Color.		Acids.		Esters.		Aldehydes.		Furfural.		Fuel		Oil.		Color tests.					
Composition of must					Proof	Original	Calculated to proof.	Original.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Calculated to proof.	Original.	Per cent. color insoluble in water.	Per cent. color soluble in amyl alcohol.	Depth of Gen. Col. cal from cols. 22, 10.	Chloroform.	Amyl alcohol.	Paraldehyde	Sum of Cong. of cols. 12, 14, 16, 18, 20		
Serial No. of package					Date of inspection					Age by years and months.																
Malts					11-9-00	7 yrs. 3 mo.	116.525	280	21.0	18.0	108.0	93.1	99.9	86.1	12.0	10.3	5.2	4.5	188.162	76	13.7	Genuine	Genuine	Genuine	356.0	
1.1.8 lbs.					26497	11-9-00	116.525	280	18.0	15.9	98.4	87.1	96.0	85.0	8.0	7.1	3.0	2.6	192.170	76	13.1	"	"	"	351.8	
1.1.8 lbs.					26498	11-9-00	116.525	280	19.7	17.5	98.4	87.0	90.1	79.7	10.0	8.9	2.6	2.3	195.172	76	13.1	"	"	"	348.9	
1.1.8 lbs.					26499	11-9-00	116.525	280	20.0	17.4	103.2	89.6	102.4	88.7	12.0	10.4	4.2	2.8	194.169	75	13.5	"	"	"	354.9	
1.1.8 lbs.					26500	11-9-00	116.525	280	20.5	17.7	105.6	90.5	95.0	81.9	11.2	9.7	3.2	2.8	202.174	77	13.5	"	"	"	359.9	
Malts					11-9-00	7 yrs. 3 mo.	116.525	280	21.0	18.0	108.0	93.1	99.9	86.1	12.0	10.3	5.2	4.5	188.162	76	13.7	Genuine	Genuine	Genuine	356.0	
1.1.8 lbs.					26497	11-9-00	116.525	280	18.0	15.9	98.4	87.1	96.0	85.0	8.0	7.1	3.0	2.6	192.170	76	13.1	"	"	"	351.8	
1.1.8 lbs.					26498	11-9-00	116.525	280	19.7	17.5	98.4	87.0	90.1	79.7	10.0	8.9	2.6	2.3	195.172	76	13.1	"	"	"	348.9	
1.1.8 lbs.					26499	11-9-00	116.525	280	20.0	17.4	103.2	89.6	102.4	88.7	12.0	10.4	4.2	2.8	194.169	75	13.5	"	"	"	354.9	
1.1.8 lbs.					26500	11-9-00	116.525	280	20.5	17.7	105.6	90.5	95.0	81.9	11.2	9.7	3.2	2.8	202.174	77	13.5	"	"	"	359.9	
Malts					11-9-00	7 yrs. 3 mo.	116.525	280	21.0	18.0	108.0	93.1	99.9	86.1	12.0	10.3	5.2	4.5	188.162	76	13.7	Genuine	Genuine	Genuine	356.0	
1.1.8 lbs.					26497	11-9-00	116.525	280	18.0	15.9	98.4	87.1	96.0	85.0	8.0	7.1	3.0	2.6	192.170	76	13.1	"	"	"	351.8	
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In the last column of the analytical sheet is recorded the sum of the congeneric substances.

The data for the samples taken from the packages in suit, or as they will be spoken of from now on, the suspected samples, is printed in heavy type.

The data for the samples taken from packages in the U. S. bonded warehouses of the respective distilleries, and, therefore, authentic samples, which will be spoken of as genuine samples, is recorded in light type.

The experimental work in this office had proved the following point: that when whiskey is stored in charred oak barrels in dry storage, the proof, solids, color and the different congeneric substances increase in proportion to the time stored. While this basic principle was admitted by nearly every one interested, it was contended by the attorneys for the wholesale liquor dealers, before mentioned, that while the increase was proportional to the time stored, yet there was no relation between the increase in different packages of the same age, or any age. In other words, their claim was that while these constants did increase, yet the increase was not regular, and because one package four years old contained certain amounts of acids, esters, etc., another package of the same age would contain entirely different proportions and amounts of acids, esters, etc.

An examination, by the writer, of the two distilleries whose marks and brands were on the packages under seizure showed that at that time, Fall of 1908, every effort was being made to produce a clean new whiskey; that this was reduced to proof and bonded in charred white oak barrels of the best cooperage obtainable; that the usual warehouse care was given the whiskey the moment it was placed in the warehouse; that the warehouses were subjected to a normal temperature of from 70° to 80° F.; that the aim of the distillers, in each case, was to produce a whiskey commercially as near as possible to their own standard.

Samples from Distillery "A" are divided into nine groups, representing whiskey of different ages. The suspected samples are placed in the group where they belong according to the age indicated by the marks and brands.

In the group which is four years and one month old we were fortunate in obtaining five samples which were inspected the same date as one of the suspected samples, namely, package No. 50,715, and, therefore, the contents of these packages were taken from the same cistern on the date they were inspected, and on that date, if the contents of the cistern had been thoroughly mixed, the whiskey in each package had identically the same composition as each and every other package. As the proof in each package was the same, the contents of the cistern had been thoroughly mixed, otherwise the proof would have varied.

Taking the packages of new whiskey we find a trace of solid matter, no color, a very small amount of acids, a larger quantity of esters, a small amount of aldehydes, practically only a trace of furfural and a considerable amount of higher alcohols. Between the two samples produced on different days and nearly

a month apart there was no appreciable difference in any of the constants, the sum of the congenics being 161.7 for one, 175.0 for the other.

In the sample one day old (which means one day in wood) we find no distinction between this and the samples just produced, except that the package one day in wood contained an appreciable amount of color.

In the sample three days old we find the solids to have increased several times more than in the sample just produced, the color is twice as much as in the sample one day in wood, the other constituents are approximately the same, a constant amount of furfural appearing in each sample (entirely due to the fact that furfural is largely extracted from the charred oak package).

The remaining samples of the new goods, namely those of five, six and eight days old bear the same relation as the samples just discussed, an appreciable increase in the solids, color and furfural, the other constants remaining the same. The minimum amount of congenics for this group is 161.7, maximum 198.7.

In addition to these a sample three months, and on seven and a half months old were taken; these admirably assisted in showing the process of aging. The solids have increased to 70 and 90 parts; the color to 5.3 and 6.9 degrees; the acids have changed to 34.8 parts for the three-month sample and 53.5 for the seven and a half months. The esters have increased to 60.3 and 53.2, the aldehydes to 11.5, the furfural showing a steady increase over the very new goods. The higher alcohols are approximately the same as when first produced. The total sum of the congenics is 240.2 and 239.2, an appreciable increase over the new goods.

These results prove: first, the uniform content of the different determinable constituents in whiskey just distilled; second, with the exception of the higher alcohols the congenics immediately begin to show an increase.

The next group of samples is two years and nine months old. Considerable time having elapsed, decided increases would be expected. The proof has increased to 105 and 106, four of the samples being 106 and one 105. The solids have increased to 133 minimum and 142 maximum, the color increase to a very appreciable degree, namely, 9.8 minimum and 10.4 maximum. The acids 67.9 minimum and 78.1 maximum, a difference between the five samples of only 10.2. The esters to 72.1 minimum and 76.1 maximum, a difference of 4.2. The aldehydes 7.1 minimum and 12.2 maximum; furfural 2.0 minimum and 4.1 maximum; higher alcohols 135 minimum and 159 maximum, a difference of 24. The total sum of the congenics is 301.4 minimum and 316.1 maximum, a difference of 15.1.

For the five samples the percentage of color insoluble in water ranges from 72 per cent. to 83 per cent. Depth of color soluble in amyl alcohol, calculated on Brewer's Scale, varies from 7.7° to 8.4°. The quantitative tests for color gave positive reaction for genuine

color, that is, there was no apparent trace of caramel or other color than that extracted from the barrels.

In the group just discussed an important change is noted, namely, an equilibrium seems to be established between the acids and the esters, it will be observed that this condition is maintained to the end of the bonded period.

The proportion between the aldehydes is fairly constant although tending to show that in some cases the influence of the package is stronger than the influence of the storage, as indicated in the one case of the aldehydes dropping to 7.2. The furfural in one package increased to 4.1 as against an average of the four packages of 2.1. It would be expected that the amount of this constant would depend upon the package, more so than upon the storage, and, that while there would be shown a general increase and ratio between the different packages, yet the maximum and minimum would vary considerably, due to the fact that the content of furfural in the charred package varies.

The next group of samples consist of six, each bearing inspection marks of the 16th of January, 1904. Five of these samples, namely, 50,723-27 inclusive, were taken from the respective packages at the U. S. Bonded Warehouses, and were four years and one month old when taken. Sample package No. 50,715 was taken from a package on the premises of the claimant of the litigation. As was mentioned previously, all packages inspected on the same day are necessarily taken from the same cistern which has been thoroughly mixed and reduced to the proper proof before a single package is filled. On this day, namely, January 16, 1904, the contents of each and every package inspected would have analyzed the same, as each was an aliquot portion of the cistern.

Four of the six samples have a proof of 105 and two a proof of 104. The solid content of the genuine samples varies from 151 to 168; the solid content of the suspected sample is 125. The depth of color in the genuine varies from 10.6 to 13.3; the color of the suspected sample is 12.4. (It is expected that in these cases when substitution has been effected, that artificial color will be added and the depth of color brought back to that of the original whiskey, at least.)

The acids of the genuine samples analyzed vary from 70.4 to 84.6, a difference of 14.2; the acids of the suspected samples 21.7, or about 48.7 points less than the minimum sample of the genuine.

The esters of the genuine vary from 65.9 to 79.1, a difference of 13.2; the esters of the suspected sample are 26.1 or 39.8 less than the minimum genuine.

The aldehydes of the genuine vary from 10.8 to 12.2; the suspected sample contains 2.3 parts.

The furfural of the genuine varies from 1.1 to 1.9; only a trace of furfural appears in the suspected.

The content of higher alcohols, of the genuine samples, varies from 132 to 163, a difference of 31; the content of the suspected samples in higher alcohol is 51 parts, or 81 parts less than the minimum genuine.

The claim is made that as the higher alcohol content

of these six packages on the day of inspection was the same, and any difference at the time of the analysis was due to evaporation and osmotic action which changes tend to increase the higher alcohol content and never diminishes it, then these results clearly show that package 50,715 contained only about one-third of the fusel oil that should be expected.

In studying the composition of the color, we find that the "color insoluble in water" of the genuine samples varies from 74 to 77 per cent.; there is no color insoluble in water in the suspected samples, all of the color dissolving in this menstruum.

The "color soluble in amyl alcohol" for the genuine varies from 76 to 87 per cent. The same test on the suspected shows only 17 per cent soluble. The depth of color soluble in amyl alcohol varies from 9.2 to 10.1; the depth of color soluble in amyl alcohol of the suspected sample is 2.1. The qualitative test for artificial coloring matter proved the color of the genuine samples to be genuine color, derived from the oak package; the same tests on the suspected samples proved a heavy artificial coloration.

The sum of the congeneric substances in the genuine samples vary from 291.3 to 337.1, a difference of 45.8 between the maximum and minimum, or samples taken from packages known to be unsophisticated; the sum of the congenics in the suspected sample is 101.1, or only one-third as much as the genuine samples.

The next group of samples analyzed are five samples taken from packages four years and eight months old, on the premises of the U. S. Bonded Warehouse. The proof in four of the samples is 112, in one 114. The solids vary from 204 to 243. The color from 14.9 to 18.3. The acids from 90.4 to 103.0. The esters from 88.4 to 115.8. The aldehydes from 10.5 to 11.4. Furfural 3.2 to 3.3. Higher alcohol 225 to 224. The color insoluble in water 76 to 82 per cent. Color soluble in amyl alcohol 74 to 80 per cent. The depth of color soluble in amyl alcohol 11.2° to 14.3°. The qualitative tests for color proved in each case to be genuine. The sum of the congeneric substances varies from 417.6 to 460.8.

The next group of samples analyzed contains whiskey five years and eight months old. Five samples inspected 6-14-02, taken from U. S. Bonded Warehouses; two samples, namely, 38,959 and 38,965, inspected three days after the samples just mentioned were taken from packages found on the premises of the claimant of the whiskey, being two of the packages in litigation. The proof of the genuine sample is 109; of the suspected samples 109 and 108 respectively. The solid contents of the genuine samples vary from 190 to 219; of the suspected samples 120 and 136. The depth of color of the genuine varies from 13.8 to 16; of the suspected 12.8 and 10.6. The acids of the genuine vary from 79.3 to 88.0; of the suspected 25.3 to 27.8. The esters on the genuine vary from 75.5 to 90.4; of the suspected 29.7 and 28.9. The aldehydes of the genuine vary from 14.7 to 17; in the suspected 4.2 and 2.6. Furfural from 1.8 to 2.2 in the genuine, and in the suspected 0.6 and 0.4. The

fusel oil found in each genuine sample varies from 168 to 208, and in the suspected samples 67 and 55, or about one-third of that amount found in the whiskey known to be genuine.

Examining the composition of the color we find that the color insoluble in water in the genuine varies from 74 to 79 per cent., on the suspected it is 90 per cent. In each case the color soluble in amyl alcohol, in the genuine, varies from 72 to 80 per cent.; in the suspected samples 26 and 25 per cent. is soluble. The depth of color soluble in amyl alcohol, in the genuine, varies from 10.5 to 11.6; in the suspected it is 3.3 and 2.6. Qualitative tests for color in the genuine prove all the color to be that extracted from the oak packages. The same tests show a heavy artificial coloration in the suspected packages.

The sum of the congeners in the genuine varies from 347.2 to 382.4, a difference of 35.2. The sum of congeners of the suspected samples is 126.8 and 114.7 or 220 points less than in the genuine package containing the smallest amount.

The next group of samples analyzed consists of fifteen samples, nine taken from the Bonded Warehouse, and six from packages found on the premises of the claimants, and therefore part of the packages in litigation.

The samples vary in age from six years and eight months to six years and eleven months.

The proof in the genuine samples varies from 111 to 115; in the suspected from 110 to 113. The solids of the genuine vary from 185 minimum to 238 maximum; the suspected from 128 to 168. The depth of color of the genuine from 13.5 to 17.5; suspected 11.0 to 14.0. The acids of the genuine vary from 83.6 minimum to 100.0 maximum; of the suspected from 34.8 to 40.8. The esters from 77.7 to 95.6, while the esters of the suspected from 27.7 to 32.5, or about one-third as high as the genuine samples of the same age. The aldehydes from 10 to 13.3; the suspected aldehyde content from 3.9 to 5.1. The furfurals varied from 1.3 to 3.1; the suspected from 0.4 to 1.1. The higher alcohols of the genuine from 153 to 233; in the suspected from 46 to 68, about one-third as high as the content of the authentic samples.

The color insoluble in water of the genuine from 72 to 79 per cent.; of the suspected 5.0 to 29 per cent. The color soluble in amyl alcohol from 80 to 86 per cent.; in the suspected from 26 to 33 per cent. The depth of color soluble in amyl alcohol from 11.1° to 14.5° for the genuine, 3.4 to 4.0 for the suspected. The qualitative tests proved no artificial color in the genuine samples, while a large amount of caramel was indicated as present in the suspected.

The sum of the congeners of the genuine vary from 335.4 to 430.7; the suspected from 111.3 to 134.9, or the same difference as indicated in the other comparisons.

The last group analyzed consisted of five samples seven years and three months old in wood.

The proof varies from 113 to 116. The solids from 220 to 280. The depth of color from 15.9 to 18.

The acids from 87.0 to 93.1. The esters from 70 to 88.7. The aldehydes from 7.1 to 10.4. The furfurals from 2.3 to 4.5. The higher alcohols from 1 to 174. The color insoluble in water 73 to 77 per cent. The color soluble in amyl alcohol from 72 to 84 per cent. The depth of color soluble in amyl alcohol from 11.4 to 13.7. The sum of the congeners from 348.9 to 361.4.

A careful examination of this résumé of the table and the curves should convince one of the following points concerning the whiskey taken from the U. S. Bonded Warehouse and described herein as genuine.

1. That there is a general tendency in the proof, color, solids, and the congeners to increase the longer the storage.

2. That the results prove this increase to be uniform and comparable in packages of approximately the same age, the variation being almost negligible when taking into consideration the possible variation between two different determinations.

3. That the individual package seems to have no other influence (in this connection) than to cause a slight variation in the depth of color and the amount of aldehydes. The content of furfural depends almost entirely on the package and the length of storage.

4. The composition of the color extracted is the same in all the packages, never less than 70 per cent. insoluble in water, or the same per cent. soluble in amyl alcohol (note about Marsh test).

As regards the suspected samples they are not similar to the genuine samples in any points, except proof and depth of color.

The following is the examination of a so-called "Neutral" spirit, or "Blending Goods:"

	Grams per 100 liters.
Proof, 100 per cent.....	Acids..... 13.3
Color, water white.....	Esters..... 20.4
Odor, neutral.....	Higher alcohols..... 6.3
	Aldehydes..... 0.5
	Furfural..... 0.0

This is the class of goods frequently used in the kind of manipulation (substitution) and if used the proportion of two parts of neutral spirits to one of the real whiskey, brought to the proper degree of proof and colored with caramel, until the deficiency in the color, caused by the water white spirit is made up, will give upon analysis figures very similar to the whiskey called suspected herein.

I will not consider in such detail the analysis of the whiskey taken from the distillery designated here as Distillery "B," and of the four packages in litigation bearing marks and brands of this distillery, but suspected of containing other spirits.

These packages were proceeded against in order to introduce evidence in the analytical data of samples from another distillery located in another section of the country where different local conditions might exist. In this case the whiskey in litigation was supposed to be eight years and ten months old, or ten months older than the law permits whiskey to remain in bond; thus it was impossible to obtain samples from the warehouse nearer than ten months

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27																
Name			Total No. of packages		Date of inspection		Age, by years and months		Proof		Original		Calculated to proof		Original		Calculated to proof		Original		Calculated to proof		Original		Calculated to proof		Per cent. color insoluble in water.		Per cent. color soluble in amyl alcohol.		Depth of Gen. Col. cal. from cols. 22, 10.		Chloroform.		Amyl alcohol.		Paraldehyde.		Sum of Cong. sub. columns 12, 14, 18, 20.		Line No.	
1	340 bu. 60 bu.	28890	4 24 99	8 yrs. 10 mo.	115	164	142	16 5	14 3	49 2	42 8	66 0	48 7	8 0	6 9	2 2	1 9	70 0	61 0	17 29	29	4 1	Caramel Heavy	161 3	1																	
2	340 bu. 60 bu.	28891	4 24 99	8 yrs. 10 mo.	116	134	115	17 0	14 5	48 0	41 4	68 1	50 1	7 6	6 5	2 2	2 4	61 0	52 0	17 26	36	3 6	Caramel Heavy	157 4	2																	
3	340 bu. 60 bu.	28892	4 24 99	8 yrs. 10 mo.	118	134	115	17 0	14 5	48 0	41 4	68 1	50 1	7 6	6 5	2 2	2 4	61 0	52 0	17 26	36	3 6	Caramel Heavy	157 4	3																	
4	340 bu. 60 bu.	28893	4 24 99	8 yrs. 10 mo.	118	134	115	17 0	14 5	48 0	41 4	68 1	50 1	7 6	6 5	2 2	2 4	61 0	52 0	17 26	36	3 6	Caramel Heavy	157 4	4																	
5	340 bu. 60 bu.	28894	4 24 99	8 yrs. 10 mo.	118	134	115	17 0	14 5	48 0	41 4	68 1	50 1	7 6	6 5	2 2	2 4	61 0	52 0	17 26	36	3 6	Caramel Heavy	157 4	5																	
6	340 bu. 60 bu.	28895	4 24 99	8 yrs. 10 mo.	118	134	115	17 0	14 5	48 0	41 4	68 1	50 1	7 6	6 5	2 2	2 4	61 0	52 0	17 26	36	3 6	Caramel Heavy	157 4	6																	
7	340 bu. 60 bu.	28896	4 24 99	8 yrs. 10 mo.	117	236	202	16 5	14 1	102 0	87 2	96 8	82 7	8 8	7 5	6 0	5 1	135 0	132 0	18 78	11 0	9 7	Caramel Heavy	155 4	7																	
8	340 bu. 60 bu.	28897	4 24 99	8 yrs. 10 mo.	119	250	210	16 5	14 1	109 2	91 2	111 1	93 4	11 6	9 7	5 6	4 3	128 0	108 0	75 82	11 2	9 7	Caramel Heavy	139 4	8																	
9	340 bu. 60 bu.	28898	4 24 99	8 yrs. 10 mo.	118	262	222	17 0	14 4	108 2	91 2	103 4	87 6	14 0	11 9	5 6	4 7	137 0	116 0	78 80	11 2	9 7	Caramel Heavy	139 4	9																	
10	340 bu. 60 bu.	28899	4 24 99	8 yrs. 10 mo.	118	234	192	16 0	13 5	100 8	85 4	105 1	89 0	11 2	9 7	5 6	4 7	137 0	116 0	78 80	11 2	9 7	Caramel Heavy	139 4	10																	
11	340 bu. 60 bu.	28900	4 24 99	8 yrs. 10 mo.	119	232	192	15 7	13 2	99 6	83 7	108 2	89 3	8 8	7 4	5 5	4 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	11																	
12	340 bu. 60 bu.	28901	4 24 99	8 yrs. 10 mo.	121	231	192	15 7	13 0	93 6	77 4	91 0	75 0	10 0	7 6	5 5	4 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	12																	
13	340 bu. 60 bu.	28902	4 24 99	8 yrs. 10 mo.	121	241	199	15 7	13 0	93 6	77 4	91 0	75 0	10 0	7 6	5 5	4 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	13																	
14	340 bu. 60 bu.	28903	4 24 99	8 yrs. 10 mo.	120	236	188	15 5	12 4	100 8	72 0	85 3	73 2	9 2	7 6	5 5	4 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	14																	
15	340 bu. 60 bu.	28904	4 24 99	8 yrs. 10 mo.	113	205	185	13 5	12 0	81 6	64 3	85 3	73 2	7 5	6 0	5 1	135 0	132 0	18 78	11 0	9 7	Caramel Heavy	157 4	15																		
16	340 bu. 60 bu.	28905	4 24 99	8 yrs. 10 mo.	113	210	186	13 3	12 1	82 1	64 3	85 3	73 2	7 5	6 0	5 1	135 0	132 0	18 78	11 0	9 7	Caramel Heavy	157 4	16																		
17	340 bu. 60 bu.	28906	4 24 99	8 yrs. 10 mo.	114	197	173	13 7	12 0	84 0	64 3	85 3	73 2	7 5	6 0	5 1	135 0	132 0	18 78	11 0	9 7	Caramel Heavy	157 4	17																		
18	340 bu. 60 bu.	28907	4 24 99	8 yrs. 10 mo.	116	211	182	15 0	12 9	93 6	80 7	78 2	73 2	10 8	9 2	7 6	5 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	18																	
19	340 bu. 60 bu.	28908	4 24 99	8 yrs. 10 mo.	113	196	173	14 0	12 4	84 0	74 3	78 2	69 2	10 8	9 2	7 6	5 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	19																	
20	340 bu. 60 bu.	28909	4 24 99	8 yrs. 10 mo.	113	192	170	15 0	13 3	84 0	74 3	78 2	69 2	10 8	9 2	7 6	5 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	20																	
21	340 bu. 60 bu.	28910	4 24 99	8 yrs. 10 mo.	114	209	183	15 5	13 0	92 4	81 6	80 3	70 6	11 4	10 2	7 4	5 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	21																	
22	340 bu. 60 bu.	28911	4 24 99	8 yrs. 10 mo.	116	218	194	16 0	13 0	102 0	82 6	79 2	68 9	12 0	10 8	9 2	7 6	5 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	22																
23	340 bu. 60 bu.	28912	4 24 99	8 yrs. 10 mo.	116	221	234	18 0	13 4	92 4	80 4	79 2	68 9	12 0	10 8	9 2	7 6	5 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	23																
24	340 bu. 60 bu.	28913	4 24 99	8 yrs. 10 mo.	115	222	193	17 2	13 4	92 4	80 4	79 2	68 9	12 0	10 8	9 2	7 6	5 5	133 0	110 0	75 76	11 3	9 7	Caramel Heavy	157 4	24																
25	340 bu. 60 bu.	28914	4 24 99	8 yrs. 10 mo.	112	214	191	16 0	13 1	90 0	78 5	84 5	73 4	15 2	13 6	3 2	2 5	234 0	209 0	80 76	10 5	9 8	Caramel Heavy	157 4	25																	
26	340 bu. 60 bu.	28915	4 24 99	8 yrs. 10 mo.	114	202	181	15 0	13 1	84 8	73 7	76 6	61 2	15 2	13 6	3 2	2 5	234 0	209 0	80 76	10 5	9 8	Caramel Heavy	157 4	26																	
27	340 bu. 60 bu.	28916	4 24 99	8 yrs. 10 mo.	114	202	181	15 0	13 1	84 8	73 7	76 6	61 2	15 2	13 6	3 2	2 5	234 0	209 0	80 76	10 5	9 8	Caramel Heavy	157 4	27																	
28	340 bu. 60 bu.	28917	4 24 99	8 yrs. 10 mo.	111	198	171	14 0	12 6	80 4	64 6	80 9	72 2	12 0	10 7	12 0	1 8	223 0	199 0	73 82	10 3	9 8	Caramel Heavy	157 4	28																	
29	340 bu. 60 bu.	28918	4 24 99	8 yrs. 10 mo.	112	200	176	13 7	12 0	82 2	64 6	80 9	72 2	12 0	10 7	12 0	1 8	223 0	199 0	73 82	10 3	9 8	Caramel Heavy	157 4	29																	
30	340 bu. 60 bu.	28919	4 24 99	8 yrs. 10 mo.	112	200	176	13 7	12 0	82 2	64 6	80 9	72 2	12 0	10 7	12 0	1 8	223 0	199 0	73 82	10 3	9 8	Caramel Heavy	157 4	30																	
31	340 bu. 60 bu.	28920	4 24 99	8 yrs. 10 mo.	112	198	178	15 0	13 0	86 2	77 1	82 2	64 6	11 6	10 4	10 4	1 6	235 0	213 0	71 76	10 3	9 8	Caramel Heavy	157 4	31																	
32	340 bu. 60 bu.	28921	4 24 99	8 yrs. 10 mo.	112	198	178	15 0	13 0	86 2	77 1	82 2	64 6	11 6	10 4	10 4	1 6	235 0	213 0	71 76	10 3	9 8	Caramel Heavy	157 4	32																	
33	340 bu. 60 bu.	28922	4 24 99	8 yrs. 10 mo.	112	198	178	15 0	13 0	86 2	77 1	82 2	64 6	11 6	10 4	10 4	1 6	235 0	213 0	71 76	10 3	9 8	Caramel Heavy	157 4	33																	
34	340 bu. 60 bu.	28923	4 24 99	8 yrs. 10 mo.	112	198	178	15 0	13 0	86 2	77 1	82 2	64 6	11 6	10 4	10 4	1 6	235 0	213 0	71 76	10 3	9 8	Caramel Heavy	157 4	34																	
35	340 bu. 60 bu.	28924	4 24 99	8 yrs. 10 mo.	112	198	178	15 0	13 0	86 2	77 1	82 2	64 6	11 6	10 4	10 4	1 6	235 0	213 0	71 76	10 3	9 8	Caramel Heavy	157 4	35																	
36	340 bu. 60 bu.	28925	4 24 99	8 yrs. 10 mo.	112	198	178	15 0	13 0	86 2	77 1	82 2	64 6	11 6	10 4	10 4	1 6	235 0	213 0	71 76	10 3	9 8	Caramel Heavy	157 4	36																	
37	340 bu. 60 bu.	28926	4 24 99	8 yrs. 10 mo.	112	198	178	15 0	13 0	86 2	77 1	82 2	64 6	11 6	10 4	10 4	1 6	235 0	213 0	71 76	10 3	9 8	Caramel Heavy	157 4	37																	
38	340 bu. 60 bu.	28927	4 24 99	8 yrs. 10 mo.	112	198	178	15 0	13 0	86 2	77 1	82 2	64 6	11 6	10 4	10 4	1 6	235 0	213 0	71 76	10 3	9 8	Caramel Heavy	157 4	38																	
39	340 bu. 60 bu.	28928	4 24 99	8 yrs. 10 mo.	111	193	174	15 2	13 7	84 0	75 7	78 3	71 0	10 8	9 7	1 2	1 1	216 0	194 0	70 76	10 4	9 8	Caramel Heavy	157 4	39																	
40	340 bu. 60 bu.	28929	4 24 99	8 yrs. 10 mo.	102	162	161	14 7	13 7	84 0	75 7	78 3	71 0	10 8	9 7	1 2	1 1	216 0	194 0	70 76	10 4	9 8	Caramel Heavy	157 4	40																	
41	340 bu. 60 bu.	28930	4 24 99	8 yrs. 10 mo.	108	213	164	15 4	14 3	86 4	80 5	70 0	61 7	9 2	8 0	6 9	5 8	98 0	72 0	71 80	10 3	9 8	Caramel Heavy	157 4	41																	
42	340 bu. 60 bu.	28931	4 24 99	8 yrs. 10 mo.	108	213	164	15 4	14 3	86 4	80 5	70 0	61 7	9 2	8 0	6 9	5 8	98 0	72 0	71 80	10 3	9 8	Caramel Heavy	157 4	42																	
43	340 bu. 60 bu.	28932	4 24 99	8 yrs. 10 mo.	108	213	164	15 4	14 3	86 4	80 5	70 0	61 7	9 2	8 0	6 9	5 8	98 0	72 0	71 80	10 3	9 8	Caramel Heavy	157 4	43																	
44	340 bu. 60 bu.	28933	4 24 99	8 yrs. 10 mo.	107	194	181	13 5	14 3	80 4	73 1	62 7	33 4	8 8	8 2	2 2	1 3	84 0	83 0	73 74	10 6	10 7	Caramel Heavy	157 4	44																	
45	340 bu. 60 bu.	28934	4 24 99	8 yrs. 10 mo.	109	149	137	11 5	10 5	61 2	56 1	37 4	38 3	8 4	7 7	1 8	1 6	92 0	84 0	72 80	8 4	10 7	Caramel Heavy	157 4	45																	
46	340 bu. 60 bu.	28935	4 24 99	8 yrs. 10 mo.	110	169	158	12 5	13 2	72 0	66 1	43 5	33 9	8 4	7 7	1 8	1 6	92 0	84 0	72 80	8 4	10 7	Caramel Heavy	157 4	46																	
47	340 bu. 60 bu.	28936	4 24 99	8 yrs. 10 mo.	110	174	158	12 5	13 2	72 0	66 1	43 5	33 9	8 4	7 7	1 8	1 6	92 0	84 0	72 80	8 4	10 7	Caramel Heavy	157 4	47																	
48	340 bu. 60 bu.	28937	4 24 99	8 yrs. 10 mo.	110	174	158	12 5	13 2	72 0	66 1	43 5	33 9	8 4	7 7	1 8	1 6	92 0	84 0	72 80	8 4	10 7	Caramel Heavy	157 4	48																	
49	340 bu. 60 bu.	28938	4 24 99	8 yrs. 10 mo.	108	157	170	14 0	12 7	62 4	56 7	38 7	35 2	6 0	5 3	2 6	2 4	123 0	109 0	78 84	10 7	10 7	Caramel Heavy	157 4	49																	
50	340 bu. 60 bu.	28939	4 24 99	8 yrs. 10 mo.	108	157	170	14 0	12 7	62 4	56 7	38 7	35 2	6 0	5 3</																											

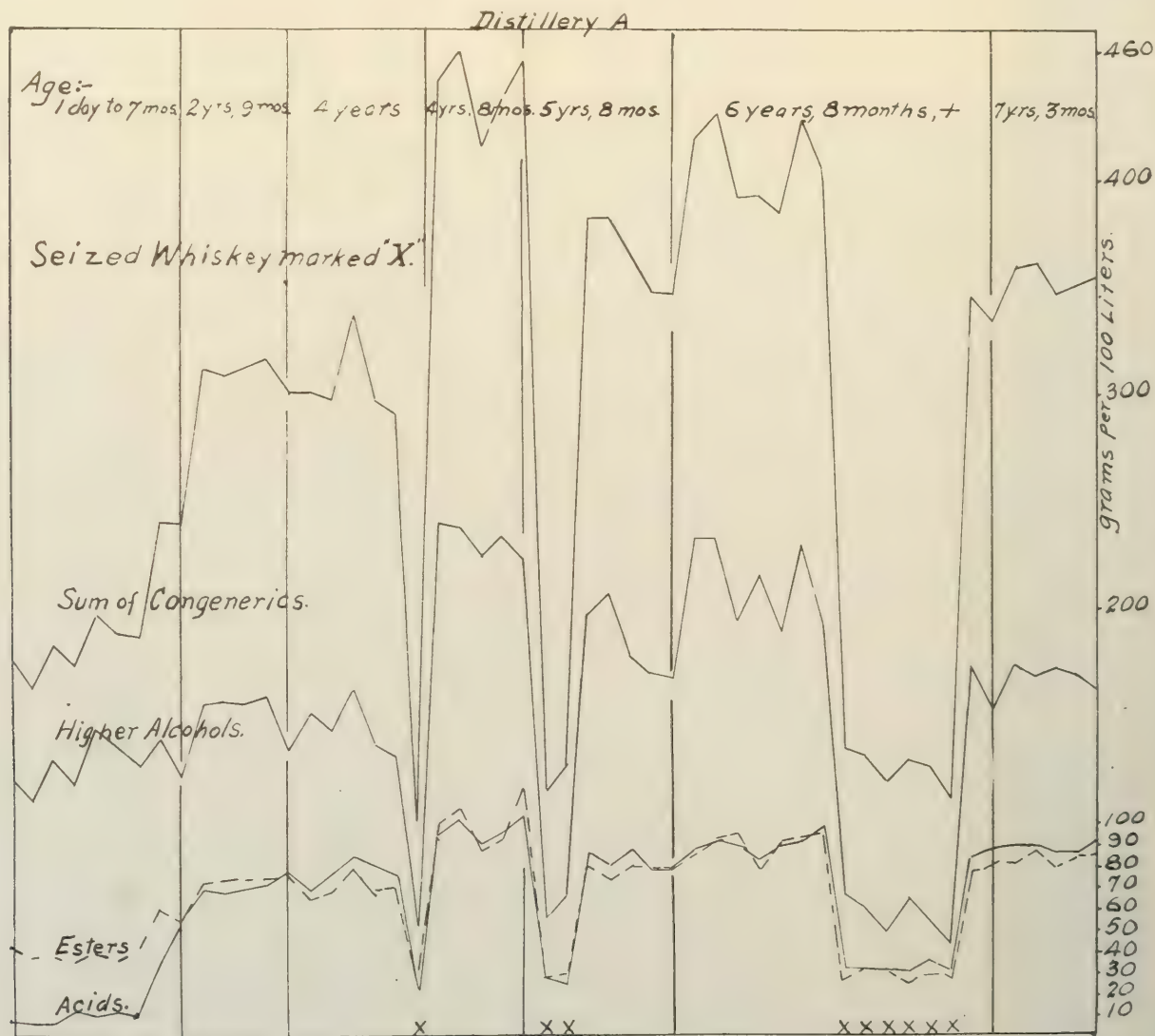
or a year; the proposition, therefore, evolved itself into proving that the product of this distillery when aged in its own warehouse contained certain amounts of color, solids and the different congeners, and that the contents of one package were comparable chemically to the contents of another package of approximately the same age.

A careful perusal of the analytical table and the curves proves essentially the same points as for Distillery "A." One marked variation developed, namely, in the higher alcohol content in the samples produced during the Fall of 1903, when nearly twice as much

A comparison of the *suspected* and the *genuine* will prove that the spirits in the four packages are not similar to the genuine and younger goods analyzed. The content of acids in the suspected is less than in the two-year goods. The content of esters less than in the three-year goods. The higher alcohols are less than for even the new goods.

All comparison ceases here and the differences become more glaring the older the whiskey becomes.

In conclusion it should be stated that in work of this kind, the acids, esters and color form the points which should be used to determine the authenticity of



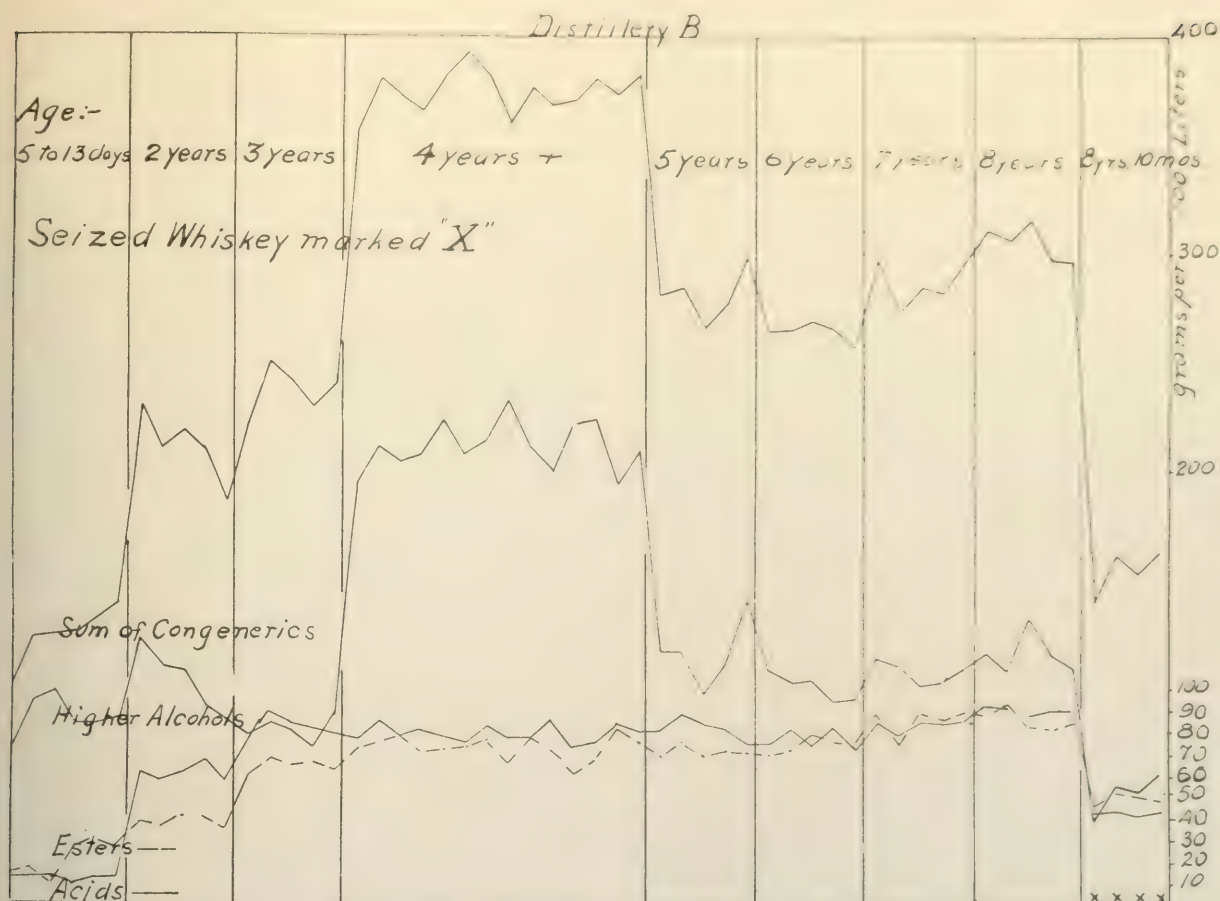
higher alcohols were produced as at any other period. (The distiller, Mr. ———, suggested that as the rye was of poor quality that year, this might account for the high amount. I am inclined to think his suggestion is a good one.) This exception, of course, is repeated in the sum of the congeners. This result would tend to show that while storage has an effect on the quantity of the higher alcohols (they increasing by concentration), yet the amount present depends more on the fermentation and the method of distillation.

the contents of a package of whiskey. The content of solids, higher alcohols, aldehydes and furfural will assist in arriving at a conclusion, but should not be relied upon solely, as can be done in the case of the acids, esters and color.

HISTORY OF THE CASE.

Trial began April 6, 1909, and ended April 14, 1909

Jury returned verdict for the Government deciding that the packages did contain other spirits than those tax-paid therein.



Submitted to Circuit Court of Appeals, June 15, 1910, decided by Circuit Court of Appeals, July 13, 1910. Reported in "Federal Reporter," Vol. 181, pages 296-306.

The Higher Court decided that:

"We are satisfied that under the evidence the jury was warranted in finding that the nine barrels in question contained distilled spirits other than the contents which were in them when they were lawfully stamped, etc.....if the testimony offered by the Government is competent." Further on in the opinion: "We conclude that the conditions under which the contents of the seized barrels and the contents of the barrels taken for comparison were produced and handled were sufficiently similar to justify the admission of the evidence objected to."

The case was remanded for a new trial as the Government did not prove that the claimants *received* the packages in the illegal condition as stated in the libel. The case will not be retried, the Government having obtained a favorable decision on the two main points at issue, namely:

1. Can the presence of other spirits in a package of double stamped whiskey be proven by chemical analysis?
2. Are the analyses of samples taken from packages in the same warehouse proper evidence against similar whiskey under seizure?

THE RELATION OF NITRATE OF SODA TO THE MECHANICAL CONDITION OF COMMERCIAL FERTILIZERS.¹

By JACOB G. LIPMAN

Received May 1, 1911

The increasing cost of organic ammoniates and the inert character of a considerable proportion of the materials (used in the making up of commercial mixtures) are forcing progressive farmers to resort, more and more, to home mixing. Those who have learned to use purchased plant food with discretion have realized that the better sources of animal and vegetable nitrogenous substances like dried blood, concentrated tankage, dried and ground fish, and cottonseed-meal have become economic luxuries. But, expensive as are these so-called high-grade materials as a source of nitrogen to crops, they are cheap as measured against the lower grades of tankage, dried blood, and, more particularly, of garbage tankage, leather scrap, hair and wool waste and peat.

It is a fact, indisputably established by almost innumerable experiments and observations, that different materials used as sources of nitrogen to crops vary in their *availability*. Otherwise, stated, some of these substances furnish a large part of their nitrogen to growing crops; that is, they are *readily available*, while others yield up but a small portion of their nitrogen within one or two growing seasons; that is, they are *slightly available*. The question of the rela-

¹ Laboratory: New Jersey Agricultural Experiment Station

tive availability of different nitrogenous plant foods has been studied extensively for several decades in Europe, as well as in the United States. We owe much of our knowledge of this subject to the painstaking researches of Wagner and of his associates at Darmstadt, and elsewhere in Germany.¹ Their results have been substantially confirmed by similar investigations in nearly every European country as well as by those in the United States.²

Taken in their entirety, the results of the many availability studies point clearly to the superiority of nitrates over all other nitrogen compounds as a source of this constituent to vegetation. For instance, in the New Jersey experiments³ it was found that with the crop returns from sodium nitrate taken at 100 the corresponding returns from ammonium sulphate were slightly less than 70, while the returns from dried blood were rather less than 65. It is evident, therefore, that because of its lesser availability the nitrogen in dried blood is worth only two-thirds as much as the nitrogen in the form of sodium nitrate.

Unfortunately for the farmer, the relative agricultural values brought out by the experiments and observations already alluded to are not reflected in the commercial values of nitrogenous plant foods. As is shown by the fertilizer bulletins of our experiment stations, nitrogen in organic forms costs much more than the equivalent quantities of nitrogen in the form either of sodium nitrate or of ammonium sulphate. For example, a recent bulletin of the New Jersey Experiment Station⁴ shows that nitrate nitrogen was purchased in the state in 1910 at an average price of 15.77 cents per pound, and ammonia nitrogen at an average price of 15.54 cents per pound. On the other hand, dried blood nitrogen was purchased at an average price of 20.25 cents per pound, and dried fish and tankage nitrogen at an average price of nearly 20 cents per pound. In some instances the purchase price exceeded 25 cents per pound. To make matters worse, the same and higher prices are charged in mixed goods for nitrogen derived from inert materials, whose relative availability is at times as low as 10 or 20 when the returns from equivalent amounts of nitrate nitrogen are taken at 100.

In view of the facts outlined above it is pertinent to ask why organic ammoniates, some of them of questionable utility, continue to command (in the open market) prices entirely out of keeping with their true agricultural value. To understand the answer to this question it should be remembered: (1) That a large quantity of such materials is purchased by the manufacturers of mixed fertilizers; (2) that they are valuable in imparting a desirable

mechanical condition to the mixed goods; (3) that they contain a relatively large proportion of nitrogen so that their addition to other materials does not lower the proportion of nitrogen in the mixture to too great an extent. On the other hand, the use of much nitrate of soda in fertilizer mixtures is objected to because (1) in the presence of acid phosphate more or less nitrogen is lost from the material; (2) the mixture tends to harden on standing, and is no longer in a condition to pass through a fertilizer drill. The longer the period of storage, the greater the loss of nitrogen, and the less satisfactory the mechanical condition of the mixture. Such being the case, the manufacturers of mixed fertilizers are naturally averse to the use of much nitrate of soda, especially since the mixtures must be made up, at times, many weeks before they are ready to be used by the farmer.

The objections to nitrate of soda, as noted above, need not apply to home mixtures. Recent experiments by C. S. Cathcart⁵ show that even in four weeks "The loss of nitrogen. . . . was not very great, and in no case was it a serious consideration." Hence, under average farm conditions, no loss need occur, since the mixing materials may be delayed until within a few days of application. Moreover, the tendency of fertilizer mixtures, containing a considerable proportion of nitrate, to harden and clog the fertilizer drill need not cause any annoyance under conditions of home mixing. Many progressive farmers use, successfully, mixtures of acid phosphate, muriate of potash and nitrate of soda, by giving due heed to climatic conditions and by delaying the mixing until within a few days of applying the fertilizer. Where, occasionally, the fertilizer mixture does harden, the material may be again crushed or ground to a fine powder without difficulty.

In order to secure additional data on the mechanical condition of mixtures of acid phosphate, muriate of potash and nitrate of soda, a number of such mixtures were prepared and tested with a view toward answering the following questions:

1. How long will mixtures of these materials remain drillable?
2. Would the addition of small amounts of dry sifted soil improve the mechanical condition of these mixtures?
3. How long will the mixtures with or without soil remain drillable?
4. Could mixtures of acid phosphate, muriate of potash, and nitrate of soda be crushed again, and made drillable, after they had hardened in storage?

The three materials were mixed in the following proportions:

260 pounds nitrate of soda.
540 pounds acid phosphate.
200 pounds muriate or sulphate of potash.

The mixed material was divided into 50-pound lots as follows:

¹ "The Use of Nitrate of Soda in Commercial Fertilizers," *THE JOURNAL*, 3, 30.

¹ See "Die Stickstoffdüngung der landwirtschaftlichen Kulturpflanzen," Berlin, 1892; "Die Düngung mit Schwefelsauren Ammoniak und organischen Stickstoffdüngungen in Vergleich zum Chilisalpeter," Heft 80, "der Deutschen Landwirtschafts-Gesellschaft; Versuche über die Stickstoffdüngung der Kulturpflanzen," *Ibid.*, Heft 129.

² See "Investigations Relative to the Use of Nitrogenous Materials 1898-1907," *Bull.* 221, N. J. Expt. Sta.

³ *Loc. cit.*, p. 34.

⁴ "Analyses and Valuation of Commercial Fertilizers," *Bull.* 233, N. J. Expt. Sta.

- (1) 50 pounds muriate mixture.
- (2) 50 pounds muriate mixture + 5 pounds soil.
- (3) 50 pounds muriate mixture + 10 pounds soil.
- (4) 50 pounds muriate mixture + 15 pounds soil.
- (5) 50 pounds sulphate mixture
- (6) 50 pounds sulphate mixture + 5 pounds soil.
- (7) 50 pounds sulphate mixture + 10 pounds soil.
- (8) 50 pounds sulphate mixture, + 15 pounds soil.

Each of these mixtures was represented by three portions. The bags and contents were stored in a dry, cool place, and one lot of each was drilled at the end of 1, 2 and 3 weeks, respectively. Determinations of moisture were made in the ingredients used and also in the different mixtures at stated intervals. The amounts of moisture found were as follows:

MOISTURE CONTENT OF SINGLE INGREDIENTS AND OF THE MIXTURES.

Samples taken. Samples marked.	Calculated.					
	Per cent.	Per cent.	2/11/11 2/14/11	2/18/11 2/20/11	2/25/11 2/27/11	3/4/11 3/6/11
Acid phosphate.....	13.05
K ₂ SO ₄	9.18
KCl.....	1.53
NaNO ₃	3.98
Soil.....
KCl mixture.....	8.39	10.36	10.00	10.00	9.95	9.95
50 lbs. mixture + 5 lbs. soil..	8.33	9.70	9.61	9.03	9.58	9.58
50 lbs. mixture + 10 lbs. soil..	8.26	9.55	9.15	9.18	9.23	9.23
50 lbs. mixture + 15 lbs. soil..	8.20	9.38	9.27	9.13	8.82	8.82
K ₂ SO ₄ mixture.....	9.92	10.48	10.08	9.75	10.00	10.00
50 lbs. mixture + 5 lbs. soil..	9.84	10.33	9.65	9.45	9.80	9.80
50 lbs. mixture + 10 lbs. soil..	9.77	9.98	9.45	9.75	9.10	9.10
50 lbs. mixture + 15 lbs. soil..	9.69	9.56	9.35	9.43	9.03	9.03

As shown by the moisture determinations, the mixtures of acid phosphate, muriate of potash and nitrate of soda, with or without soil, gained a slight amount of water over the calculated. On the other hand, the corresponding mixtures containing their potash in the form of sulphate lost a slight amount of water in some instances. The differences were not great, however.

At the end of 1, 2 and 3 weeks, respectively, 50 pounds of each mixture were passed through a McWhorter fertilizer drill. No difficulty was experienced in drilling the material at any time, but it was noticed that where soil was added to the fertilizer, the mixed material passed somewhat more rapidly through the drill. A further examination of the mixtures was made at the end of 8 weeks, and it was found then that the contents of the bags could be readily crushed into fairly small particles.

In view of the foregoing statements it appears entirely feasible to make up home mixtures of acid phosphate, muriate of potash and nitrate of soda, a combination that, under average climatic and soil conditions, is sure to give the farmer the greatest amount of available plant food, for the money invested. Beyond that nitrate of soda should find more extensive use at the factory provided that slovenly methods be eliminated and wet mixing restricted. It is to be hoped, at any rate, that nitrate of soda, sulphate of ammonia, cyanamid and organic nitrogenous substances will be used in the future with rather more discrimination as to their relative agricultural values. It is to be hoped also that the

consumer of fertilizers will realize more strongly than he does to-day that a satisfactory mechanical condition is often secured, at too great a cost; and that in his anxiety to provide mixtures that will remain drillable for weeks or months the manufacturer uses substances that he would not otherwise employ.

[FROM THE LABORATORY OF FERTILITY INVESTIGATIONS]

STUDIES IN ORGANIC SOIL NITROGEN.¹

By ELMER C. LATHROP AND BARLETT F. HARRIS

Received May 15, 1911.

The question of soil nitrogen, of the forms in which it exists in the soil and of how it becomes available to plants, is one of economic interest and importance to agriculture. The nitrogen in forms recognized as readily available to plants is in normal soils low, being less than 10 per cent. of the total nitrogen present. The largest part of the nitrogen in soils exists in complex organic forms about which little is definitely known. It is obvious that a knowledge of the different ways in which this organic nitrogen is combined will prove to be of value. Two methods of attacking this problem present themselves: the application to the soil of such analytical methods as will show in a general way in what class of compounds the nitrogen exists, or, the actual isolation from the soil of organic compounds containing the nitrogen. It is the purpose of the present paper to deal with the first of these modes of attack, namely, the application of the analytical method.

The sources of the organic soil nitrogen are many and varied. Each year a large amount of organic matter, consisting of plants, plant roots, leaves, organic material in manures and in fertilizers, etc., finds its way into the soil. It is safe to say that a large part, if not all, of the nitrogen in this organic matter has been a component part of the protoplasm of the plant or animal. As soon as such organic material becomes incorporated in the soil and becomes subject to the many transforming agencies in the soil, it begins to undergo decomposition. We have, therefore, to deal with protein decomposition products in the soil. When protein undergoes decomposition, the break occurs along distinct lines of cleavage. Under the influence of chemical agents, the action of dilute acids, heat, bacteria, etc., hydrolysis takes place and the complex protein molecule breaks down into compounds of a less complex nature and finally into a number of primary and secondary dissociation products. Such being the case, one should expect a parallelism between the protein dissociation products obtained by the digestive action of dilute acids on soils in the laboratory and those products formed from plant and animal constituents in the soil under field conditions.

By heating protein material with dilute acids or superheated steam, the following kinds of nitrogenous decomposition products have been recognized for the purpose of analytical classification: ammonia, diamino acids, monoamino acids, and indefinite

¹ Published by permission of the Secretary of Agriculture

"humin" bodies. We should, therefore, expect to find some or all of these classes of compounds or forms of nitrogen in the soil or in a solution from the soil after treatment with acid or steam.

A review of the literature shows that some work has been done on the subject of nitrogenous compounds in soils or allied material and should be briefly considered. Loges¹ in 1886 found that a hydrochloric acid extract of the soil gave a precipitate with phosphotungstic acid, which is generally recognized as a precipitant for nitrogenous compounds. Eggertz² found that the nitrogen content in thirteen samples of humus varied from 2.59 per cent. to 6.43 per cent. and states that the nitrogen was present in organic form and not as ammonia. Baumann³ suggested the presence of amino compounds in the soil because of the fact that by boiling the soil with hydrochloric acid, ammonia compounds not originally present in the soil were formed. Bertholet and Andre⁴ concluded that the nitrogenous bodies were chiefly insoluble amides which are easily split into ammonia and soluble amides. Warrington⁵ reports the presence of small quantities of amides in the soil. Sestin⁶ reports that a portion of the soil nitrogen was present as amino acids. Dojarinko⁷ working with the humus from seven Russian soils obtained large quantities of amino-nitrogen, 1.34 to 1.96 per cent. of the soil. In 1905, Shorey,⁸ working with an Hawaiian soil with a view to classifying the decomposition products of the nitrogenous bodies in the soil, applied the method of Osborne and Harris,⁹ a modification of the method of Hausmann,¹⁰ to the soil. He obtained in the acid solution 8.5 per cent. of the total nitrogen in the soil, more than half of which existed as "humin" nitrogen and the remainder as ammonia, diamino acids and monoamino acids. More recently, Jodidi,¹¹ working with Michigan peat, using methods of much the same nature, concludes that "the bulk of the organic nitrogen, namely, two-thirds to three-fourths, calculated upon the nitrogen in solution by boiling with acids, is present in the form of monoamino acids, about one-fourth in the form of amides and the rest of the nitrogen represents diamino acids."

Suzuki¹² reports results obtained by treating "humic" acid with boiling hydrochloric acid and then subjecting the solution obtained to esterification and fractional distillation according to Fischer's¹³ method. By such treatment he separated and identified the esters of several of the monoamino acids and obtained tests for some of the other dissociation products of protein material. Recently, Robinson¹⁴ has isolated from Michigan peat, by means of hydrolysis with

boiling acid, leucine and isoleucine. From an alkali extract of the soil, Schreiner and Shorey in the laboratories have reported the isolation of the following nitrogenous compounds: picoline carboxylic acid, xanthine,² hypoxanthine,³ arginine,⁴ histidine,⁵ cytosine⁶ and creatinine.⁷ These compounds exist in the soil as such and are not products obtained by hydrolyzing the protein material of the soil by laboratory treatment, as is the case in the above-cited investigations, but are products formed in the soil by the decomposition of organic material.

In view of the fact that the number of nitrogenous compounds isolated from soils is rather small and that the procedure for such isolation is not only difficult but also requires very large amounts of soil, a complete study of the organic nitrogen in many soils would be almost impossible. Therefore an effort was made to see if some analytical method of deriving such knowledge could be applied so that soils might be examined more readily and the examination made on a small sample.

Five soils were selected for this examination. The soils belong to the type known as Hagerstown loam and were collected from plats of the Pennsylvania State College Experiment Station. They have been under continuous cropping and treatment since 1888. Table I shows the kind of fertilizer treatment they have received for this time. The soils were sifted through a coarse sieve, air-dried and finally passed through a one-half mm. sieve. The calculations are figured on the basis of oven-dried soil. In obtaining the data for this investigation, unless otherwise stated, the methods of analysis of the Association of Official Agricultural Chemists⁹ were used. In the determination of nitrates in the soil solution the colorimetric method was used.¹⁰

TABLE I.—FERTILIZER TREATMENT OF PLATS 20, 21, 22, 23 AND 24

Plat No.	Fertilizer added per acre.
20.....	10 tons of manure added every other year.
21.....	N as dried blood = 72 pounds N. P as dissolved bone-black = 48 pounds P ₂ O ₅ . K as muriate = 100 pounds K ₂ O. Added every other year.
22.....	Manure, 6 tons; every other year.
23.....	Limestone, burnt, 2 tons; every four years.
24.....	Limestone, burnt, 2 tons; every four years.
24.....	Check plat, nothing added.

A study of Table II shows that the amounts of total nitrogen in these soils does not vary widely, there being a difference of less than 320 p. p. m. in the extremes. The soils which have received nitrogenous fertilizers are slightly higher in total nitrogen than the other two plats not so treated. The difference in total nitrogen between plats 20 and 24 is small, still plat 24 contains only about 75 per cent. as much nitrogen as plat 20. It is the nitrogen in the form

¹ Landw. Vers. Sta., **32**, 201 (1886).

² Centrib. f. agr. Chem., **1889**, 175.

³ Landw. Vers. Sta., **33**, 247 (1887).

⁴ Compt. rend., **103**, 1101 (1886).

⁵ Chem. News, **55**, 27 (1887).

⁶ Landw. Vers. Sta., **51**, 513 (1889).

⁷ Ibid., **56**, 311 (1902).

⁸ "Agr. Invest. Hawaii in 1905," Rept. Chem., p. 34.

⁹ J. Am. Chem. Soc., **25**, 323 (1903).

¹⁰ Z. physiol. Chem., **27**, 5 (1899).

¹¹ J. Am. Chem. Soc., **27**, 396 (1910).

¹² Bull. Coll. Tokio, **7**, 513 (1907).

¹³ Z. physiol. Chem., **33**, 151, 412 (1901).

¹⁴ J. Am. Chem. Soc., **33**, 564 (1911).

¹ J. Am. Chem. Soc., **30**, 1295 (1908).

² J. Biol. Chem., **8**, 391 (1910).

³ Ibid., **8**, 392 (1910).

⁴ Ibid., **8**, 383 (1910).

⁵ Ibid., **8**, 382 (1910).

⁶ Ibid., **8**, 389 (1910).

⁷ Sci., **33**, 340 (1911).

⁸ T. F. Hunt, Penn. St. Coll., Ann. Rpt., II, 1907-'08, pp. 683.

⁹ Bull. **107**, revised, Bur. Chem., U. S. Dept. Agr.

¹⁰ Schreiner and Failyer, Bull. **31**, p. 31, Bur. Soils, U. S. Dept. Agr.

of ammonia and nitrate that is commonly recognized as available to plants; the remaining nitrogen, or about 98 per cent. of the nitrogen in these soils, is of an organic nature in which condition the nitrogen is not considered to be directly available to plants.

TABLE II.—AMOUNTS OF ORGANIC AND INORGANIC NITROGEN IN THE SOILS STUDIED.

	Parts per million of oven-dried soil.			Per cent of total N in soil.		
	Total N.	Ammonia N.	Nitric N.	Organic N.	Ammonia N.	Nitric N.
20.	1317.5	28.4	1.88	1287.2	2.15	0.143
21.	1240.0	25.6	2.06	1213.4	2.06	0.161
22.	1280.0	20.6	1.88	1257.5	1.61	0.145
23.	1052.5	16.9	1.74	1033.9	1.61	0.165
24.	1000.0	16.4	2.30	981.7	1.64	0.230

In order to determine, in a general way, the manner in which this organic nitrogen is combined in the organic matter of the soil, the method of Hausmann,¹ as modified by Osborne and Harris,² was used. This method which was first applied to the soil by Shorey³ is, in short, as follows: The soil is boiled with dilute acid and the acid solution evaporated and the excess of acid removed. The nitrogen present as ammonia is determined by boiling with an excess of magnesia; the nitrogen in the magnesia precipitate, termed "humin" nitrogen, is determined by the Kjeldahl method; the dibasic nitrogen in the filtrate is separated by precipitation with phosphotungstic acid and determined by the Kjeldahl method; the monobasic nitrogen is determined by difference from the total nitrogen determined on a separate portion of the solution. In this case 100 grams of soil were boiled with 500 cc. of hydrochloric acid, sp. gr. 1.115, for three hours in a flask supplied with a reflux condenser. The solution was filtered and the filter washed with distilled water, the filtrate evaporated on the water bath to remove the excess of acid and then made up with distilled water to a volume of 500 cc. Aliquot portions of this solution were taken for analysis.

In order to study the changes in the nitrogen compounds under the influence of moist heat, the soils were treated as follows: 40 grams of soil were heated at the desired pressure with 200 cc. of distilled water for one hour. The solutions were filtered, the soil washed with distilled water, and made up to a volume of 200 cc. and the ammonia nitrogen and the total nitrogen in solution determined in aliquot portions. For the determination of the nitrogen remaining in the soil, the entire 40 grams of soil were used.

Ammonia Nitrogen.—In consideration of the dissociation products, ammonia nitrogen comes first. Nasse,⁴ as well as later investigators, agree that after the dissociation of the protein molecule, either by acids or by heat, ammonia is always present in the dissociation products. It may be stated that although the amount of ammonia obtained in the dissociation products depends on the concentration of the acid and the length of heating, that the known final cleavage products of protein do not give off ammonia by such treatment. The figures given here for ammonia

nitrogen depend on the nature of the soil. In the ammonia obtained by dissociation and do not include the ammonia nitrogen already present in the soil.

TABLE III.—PER CENT OF NITROGEN FORMED AS AMMONIA NITROGEN AND PER CENT OF NITROGEN REMAINING SOLUBLE BY STEAM DIGESTION AT 2, 4, 6, 8, AND 10 ATMOSPHERES PRESSURE. RESULTS EXPRESSED IN TERMS OF TOTAL N.

Plat. No.	Ammonia nitrogen					Soluble nitrogen					Nitrogen that is not soluble at 10 atmospheres pressure
	2	4	6	8	10	2	4	6	8	10	
20.	0.97	5.87	7.71	10.68	11.80	14.47	21.41	23.50	34.21	44.44	55.56
21.	2.31	5.62	9.85	10.97	14.45	13.67	20.01	23.82	28.30	39.09	60.91
22.	3.80	5.42	5.73	6.88	11.59	12.08	18.61	19.72	25.08	38.33	61.67
23.	3.12	3.12	3.12	3.78	7.83	10.42	13.67	16.10	22.86	37.49	62.51
24.	3.32	6.11	11.08	13.18	15.64	8.55	19.75	21.09	22.55	46.77	53.23

In Table III are given the data obtained by the digestion of the five soils under steam pressures of 2, 4, 6, 8 and 10 atmospheres and in Table IV, the data obtained by the digestion of the soils with hydrochloric acid in the manner already described. It will be seen from Table IV that the three plats, 20, 21 and 22, which have received organic fertilizers give the largest amount of ammonia on dissociation, the amount being highest in the plat which has received manure alone (20) and lowest in the check plat (24). In the pressure digestion of the soils, Table III, the majority of the soils under increased pressure show a proportional increase in the amount of ammonia nitrogen formed, as might be expected. However, in the case of the limed plat (23), the amount of ammonia formed at 2, 4 and 6 atmospheres is the same and only a small increase is obtained at 8 and 10 atmospheres. Soil 22, the other limed plat, shows a more gradual increase in ammonia, but the increase is much smaller than in the case of soils 20 and 21 which

TABLE IV.—ANALYTICAL CLASSIFICATION OF NITROGEN IN DECOMPOSITION PRODUCTS FORMED BY THE DIGESTION OF THE SOILS WITH HYDROCHLORIC ACID.

Plat No.	Per cent of total nitrogen in soil.					
	N insoluble in acid	N soluble in acid	Ammonia N.	Diamino acid N.	Monamino acid N.	Soluble "humin" N.
20.	26.29	73.71	21.64	12.97	8.63	28.32
21.	28.28	71.72	19.98	5.82	29.04	14.46
22.	28.02	71.98	18.39	9.04	17.48	25.36
23.	29.09	70.91	16.32	8.21	12.80	31.77
24.	29.04	70.60	16.05	8.82	17.80	26.39

have received organic fertilizers without lime and 24, which has received nothing. This indicates that the nitrogenous organic matter of the two limed plats is of somewhat different nature than that of the other plats and that the nitrogenous compounds have been made more resistant to decomposition by such treatment. In this connection it will also be noticed that although soils 22 and 23 show only a small increase in the amounts of ammonia formed under increasing pressure that the amounts of organic nitrogenous matter going into solution at the different pressures shows an increase comparable to that of the other soils, although the amount is not so great as in the cases of the soils not limed.

¹ Loc. cit.

² Pfüger's Arch. f. d. ges. Physiol., 6, 598 (1872); 7, 139 (1873); 8, 381 (1874).

"Humin" Nitrogen.—The compounds precipitated by the excess of magnesia from the acid solution of the soils are for the most part the so-called humin substances or melanoidins. The term "humin" was first used by Berzelius¹ in describing certain dark-colored constituents of mold. Mulder showed that on boiling protein matter with strong acid, that brown or black particles, which resemble the dark bodies of putrefying matter, separate. These bodies are also formed from many other organic compounds, including carbohydrates. However, they are uniformly high in carbon and low in hydrogen and nitrogen; they are generally insoluble in water and in acids; in alkaline solutions they are somewhat soluble and are precipitated from them by acids; they do not give any particular reactions and their decomposition products are not well defined. Samuelli² holds that the indole, pyrrol, pyridine, and tyrosine groups of the albumin molecule contribute to the formation of these compounds. In the magnesia precipitate mentioned above there would also appear other compounds containing the pyridine ring, such as picoline carboxylic acid, first isolated from an Hawaiian soil by Shorey³ and later from other soils by Schreiner and Shorey.⁴ They conclude that such a compound might possibly arise in the soil as a secondary decomposition product of the protein molecule.

It is generally considered that when the nitrogen is combined in the ring, as in pyridine compounds, that it is unavailable, and may even be harmful to plants. It would seem probable that a large part, if not nearly all of the nitrogen classed here as "humin" nitrogen, is combined in such a way as to be unavailable to plants. Table IV shows that there is over 25 per cent. of "humin" nitrogen soluble in acid from four of these soils. Soil 21 is much lower in soluble humin nitrogen than the other soils, showing only about half as much. Since the nitrogen not soluble in acid may also be considered to be "humin" nitrogen, the total amount of nitrogen in such combination is, in four soils, over 53 per cent., while in soil 21, which has received dried blood, it is only 43 per cent.

Amino Acid Nitrogen.—The two classes of amino acids have been thoroughly studied, and their nature and composition is fairly well understood. The nitrogen is in a form from which it can be readily changed into ammonia by various agents. The amino acids are resistant to the action of acids and alkalies, but the amino group may be removed by the action of enzymes and bacteria, common both to the plant and the animal. In regard to the action of bacteria on amino acids, Czapek⁵ and Emmerling⁶ have shown that the α -amino acids are excellent nutritive materials. The amino acids are acted on by bacteria in two different ways: 1. The amino acids are converted into simple acids with the elimination of ammonia. 2. Carbon dioxide is split off,

leading, as Emmerling¹ has shown, to the formation of Brieger's diamines, thus, lysine is converted into cadaverine. As a rule, the process does not stop here and the amino group is finally changed into ammonia.

That plants may use amino acids directly in their building process does not seem at all improbable. Different amino acids are present in the germinating plant seed and are used by young plants in their growth. Lefevre² has shown that in the absence of carbon dioxide plants are able to use certain amino compounds as a source of their carbon. He states that this transfer was not simply osmotic, but that these compounds were taken up by the plant roots. Work with nitrogenous compounds of this nature in water culture work in these laboratories indicates quite strongly that plants are able to use amino compounds in their building process. It would seem then that either directly or through the agency of enzymes, bacteria, etc., amino acids become available to plant use.

These soils differ rather widely in the amounts of diamino and monoamino acids which they contain, shown in Table IV, but there seems to be no agreement between the amino acid nitrogen formed and the plat treatment. However, the amino acid nitrogen as a whole represents 22 to 34 per cent. of the total nitrogen in the decomposition products of the soils.

These five samples of soil are really the same soil under long-continued treatment of different kinds. It is not improbable that work on widely different soils will show even much larger variations than those here noted. The work shows, however, that even in such cases there is a difference in the nitrogenous compounds in the soil and that different decomposition of the nitrogenous matter has and probably will continue to take place under the different conditions imposed upon the soils in the field.

BUREAU OF SOILS,
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[CONTRIBUTION FROM THE TEXAS EXPERIMENT STATION.]

AN IMPROVEMENT IN THE METHOD FOR ESTIMATING HUMUS IN SOILS.³

By J. B. RATHER.

Received May 3, 1911.

The term "humus" in this article is used to signify the ammonia-soluble organic matter of the soil, the *matierie noire* of Grandeau.⁴

The Huston and McBride⁵ modification of the Grandeau method is the present one of the Association of Official Agricultural Chemists. The chief difficulty with this method is that with some soils considerable clay is brought into suspension by the ammonia. Most of this clay cannot be removed by filtration, and upon ignition it loses water and thereby increases the quantity of organic matter which ap-

¹ Poggendorff's *Ann.*, **44**, 375 (1838).

² Hofmeister's *Beiträge*, **2**, 355 (1902).

³ Hawaii Agr. Expt. Sta., *Ann. Rpt.*, **1906**, 55.

⁴ *Bull.* **53**, p. 32, Bur. Soils, U. S. Dept. Agr.

⁵ Hofmeister's *Beiträge*, **1**, 538 (1902); **3**, 47 (1902).

⁶ *Ber.*, **35**, II, 2289 (1902).

¹ *Z. physiol. Chem.*, **29**, 334 (1900).

² *Rev. Gen. Bot.*, **18**, 145, 205, 258, 302 (1906).

³ Full details of this work will be published in *Bulletin 139* of the Texas Experiment Station.

⁴ *Compt. rend.*, **1872**, p. 988.

⁵ *Bulls.* **37** and **107** (Revised), Bureau of Chem., U. S. D. A.

parently is present. With some soils the error is so large that it is several times greater than the amount of organic matter actually present. This fault with the method has been recognized for some time and several modifications have been suggested to remedy it. The most promising of these appears to be that of Mooers and Hampton.¹ Their modification consists in evaporating the solution to dryness on a water bath and heating on the water bath for several hours. The humus is taken up with 4 per cent. ammonia and filtered. The process is repeated and the filtrate evaporated, the residue dried, weighed, and ignited as usual.

The Mooers and Hampton method has been used in this laboratory, and although a considerable amount of clay was removed, further improvement seemed desirable.

The length of time necessary to complete an analysis, when heavy clay soils are used, makes the method very long, if evaporation and solution are repeated a sufficient number of times to give a clear solution.

It is well known that salts can coagulate clay, and throw it out of suspension. Fraps and Hamner² used non-volatile salts to precipitate the clay but call attention to the fact that the salt used might be decomposed or otherwise lost on ignition. It occurred to us that a salt which volatilized or decomposed below 100° C. would overcome this difficulty. Ammonium carbonate decomposes at 85° C., and was accordingly tested for this purpose.

EXPERIMENTAL.

The methods described below were compared on twelve soils, some high and some low in humus. The solutions were prepared by washing the soils with one per cent. hydrochloric acid to remove lime, with water to remove the acid, digestion with 4 per cent. ammonia and filtration, as prescribed in the Official Method. All comparisons were made on the same solutions.

1. Humus was determined in 100 cc. by direct evaporation (Official method). The residue was dried 3 hours at 100° C., weighed, ignited and washed again.

2. One hundred cubic centimeters were evaporated to dryness on a steam bath, baked two hours, the humus redissolved in 4 per cent. ammonia and decanted from the clay. The process was repeated, the ammonia solution filtered, and the analysis completed as in the official method (1) (Mooers and Hampton method).

3. To 130 cc. of the humus solution in a glass-stoppered cylinder was added 0.650 gram (5 grams per liter) ammonium carbonate. The salt was allowed to dissolve and the solution shaken. The clay precipitate was allowed to settle over night, the clear, supernatant liquid decanted through a filter and 100 cc. evaporated, and the determination completed as in the official method. Numerous tests showed that 3 hours was a sufficient time to dry the residues. A test of the ammonium carbonate used showed that it left no residue in the above process.

RESULTS OF THE WORK.

The results are shown in the following table:

Laboratory number.		Direct evaporation (1).		Evap. and solution (2).		Precipitation of clay with ammonium carbonate (3).	
		Humus.	Ash.	Humus.	Ash.	Humus.	Ash.
114	Travis gravelly loam.....	3.35	19.43	0.78	0.95	0.58	0.21
823	Orangeburg fine sandy loam, subsoil.....	5.00	33.45	0.86	0.51	0.78	0.19
829	Houston loam.....	1.85	4.50	1.54	0.72	1.33	0.27
830	Laredo gravelly loam.....	1.70	4.81	1.11	1.18	0.90	0.28
896	Norfolk fine sandy loam...	1.28	0.66	1.32	0.69	1.20	0.57
978	Lufkin clay.....	2.15	11.00	1.29	1.97	0.95	0.47
982	Cameron clay, subsoil....	1.75	4.40	1.42	1.54	1.08	0.56
993	Orangeburg clay.....	0.86	3.97	0.58	0.35	0.45	0.37
947	Soil from alfalfa field, N. Dakota.....	6.20	13.09	5.77	3.94	5.07	0.78
941	Houston loam.....	3.14	11.95	1.25	0.55	1.07	0.20
1203	Houston clay, subsoil.....	2.18	9.51	1.00	1.53	0.83	0.45
949	Soil from an old field, Edge-ly, North Dakota.....	3.81	5.67	3.40	2.53	3.06	1.03
	Average.....	2.77	10.20	1.69	1.37	1.44	0.45
	10 per cent. correction for water in ash.....	1.75		1.55		1.39	

The amount of humus "ash" by the official method (1) varied from 3.97 per cent. (soil 993) to 33.45 per cent. (soil 823) and averaged 10.20 per cent.

The humus by the Mooers and Hampton method (2) averaged two-thirds as much as by the official method. The difference in some cases was very great. Humus in soil 823 by the official method was 5.00 per cent.; by the Mooers and Hampton method it was 0.86 per cent. The "ash" by the Mooers and Hampton method varied from 0.35 per cent. (soil 993) to 3.94 per cent. (soil 947), and averaged 1.37 per cent. This is about one-seventh as much as the average for ash by the official method.

The humus by the ammonium carbonate method (3) was lower in all cases than by the Mooers and Hampton method (2) and the ash averaged one-third as much as the ash by the latter method (2). The average for humus by the ammonium carbonate method was 1.44 per cent. and the average for ash was 0.45 per cent. This method gave very low results for ash with soils that gave a large amount of clay into suspension. With soil 823 the ash was 33.45 per cent. of the official (1) method; it was 0.51 per cent. by the Mooers and Hampton (2) method, and only 0.19 per cent. by the ammonium carbonate (3) method. With soil 114 the results for ash by methods 1, 2 and 3 are, respectively, 19.43, 0.95 and 0.21 per cent. With soil 947 the results for ash are 13.09, 3.94 and 0.78 per cent. An examination of the table shows similar differences with other soils.

When ten per cent. of the ash is subtracted from the humus results, the difference between the results by the different methods are not so great. However, this correction is purely arbitrary and represent averages. Fraps and Hamner examined a large number of soils and found that the amount of water in the clay which is held in suspension by the ammonia varied from 8 to 20 per cent. A correction, therefore, is of little value.

The above results show that the official method is

¹ J. Am. Chem. Soc., 30, 800 (1908).

² Texas Experiment Station, Bull. 129.

³ Peter and Averitt, Kentucky Experiment Station, Bull. 126, p. 53.

entirely misleading with some soils and that the Mooers and Hampton method does not remove all the suspended clay. It is possible that continued evaporation and solution would finally remove the clay from the soils we have used, but the amount of time required renders this process impracticable. During evaporation the ammonia is liable to absorb acid fumes from the laboratory and the continued baking is liable to oxidize or decompose some of the constituents of the humus.

The advantages of the method proposed by us are simplicity, speed, and the production of perfectly clear solutions.

Proposed Modification of the Official Method.—On the basis of the work just described the following modification of the official method is proposed:

Prepare the humus solution as described in the official method, and dissolve 0.65 gram ammonium carbonate in 130 cc. of the solution. Allow to stand over night in a glass-stoppered cylinder to allow the clay to settle and decant the clear supernatant liquid through a dry filter into a dry flask. Evaporate 100 cc. of the filtrate in a tared platinum dish, dry for three hours at 100°, weigh, ignite, and weigh again. Record loss on ignition as humus.

SUMMARY AND CONCLUSIONS.

1. Clay in humus solutions may be precipitated by ammonium carbonate and the precipitant disappears on evaporating the solution and drying the residue.
2. Evaporation and solution does not remove the clay completely from humus solutions.
3. Precipitation of the clay with ammonium carbonate is more nearly complete than by evaporation and solution and is a much shorter method.

THE DETERMINATION OF DUST IN BLAST-FURNACE GAS.

By WILLIAM BRADY AND L. A. TOUZALIN.

The comparatively recent introduction of gas engines for power development from blast-furnace gas, and the general realization of modern blast-furnace operators of the desirability of more thorough cleansing for gas used in stoves and boilers, has brought the iron and steel chemist face to face with the rather perplexing determination of dust in a stream of constantly flowing gas.

The writers have given this question considerable attention, and during the past five years various forms of apparatus have been constructed, many experiments have been made, and every conceivable filtering medium has been tried. It was early determined that, with a curved sampling pipe facing the flow of gas, and an extremely porous filter, fairly satisfactory comparative results could be obtained, where the gas contained less than 1.5 grains per cubic foot, by allowing the gas to flow through the filter and then through a wet test meter into the atmosphere. The static pressure of the gas alone was utilized to cause such flow, and the test was allowed to take care of itself for periods varying from eight

to twelve hours. Such tests have been run day and night for the past two years to determine the efficiency of wet scrubbers and Theisen washers. The grains of dust per cu. ft. at the entrance and exit, of any cleaning device, obtained in this way, while not ultimately correct, are comparative where the gas is not too dirty, and serve to show what the cleaning device is doing.

During the past year, however, there has been an increasing demand for some method of making dust determinations in dirty gas, which would give absolutely correct ultimate results. Tests run near the blast furnace, where the dust per cu. ft. runs higher than 1.5 grains, demonstrated that under such conditions the results obtained by merely allowing the gas to pass through the filter and deposit its dust were absolutely worthless. After encountering innumerable difficulties due to the irregularities of blast-furnace conditions the form of apparatus and method of operating to be described have been worked out, and the results appear, theoretically and practically, to be correct ultimate figures. By means of this apparatus and method of operating the same the dust may be determined in any blast-furnace gas and at any stage in its passage from the furnace to the stoves, boilers or cleaners. By means of two sets of such apparatus the efficiency of any cleaning system may be accurately determined. The results of many tests have shown that very slight changes in the construction of a dry gas cleaner may have a wonderful effect on the efficiency of the same. The value of such efficiency dust tests may, therefore, readily be appreciated.

Before the apparatus was constructed the experience of five years of preliminary work had made it clear that in working with dirty gas several important principles must be observed. These principles may be enumerated as follows:

1. In sampling gas containing solids in suspension the sample shall be withdrawn from that region of the main in which the mean velocity of the gas is found to exist.
2. In withdrawing said sample, means must be employed to change the direction of flow gradually and to cause the flow in the entrance end of the sampling pipe to be at the same velocity as the passing stream of gas.
3. Where possible, samples shall be taken from a vertical main and at least 15 feet from any bend or obstruction.
4. The gas must be filtered above 212° F. and cooled below its dew point before being delivered to the wet test meter.

In regard to Principle No. 2, it had been considered an important point to have equal velocities in the main and sampling pipe, several years before the correctness of the principle could be proved in practice. Within the last few months, the importance of observing this fundamental principle of dust determinations has been absolutely proved by tests run on gas flowing through a supply pipe to a stove. The gas was traveling at an average velocity

of 44 ft. per second. Apparatus No. 1 was inserted in the pipe and gas was withdrawn at a velocity, in the sampling pipe, of about 43 to 45 feet per second. Simultaneously, Apparatus No. 2 was inserted a few inches at the side of No. 1 and at such a point that both entrance ends of the sampling pipes were within 2 inches of each other. The gas was withdrawn through the sampling pipe of Apparatus No. 2 at about 21 to 23 feet per second. After about ten double tests had been run in this way the velocities were reversed, *i. e.*, Apparatus No. 1 was run at 21 to 23 feet per second and Apparatus No. 2 was increased to from 43 to 45 feet per second. In every test of the total run the apparatus sampling at the slower velocity showed much higher dust per cu. ft. of gas. In fact the average increase in grains of dust per cu. ft., due to slow sampling, was over 44 per cent. This test demonstrated that where a retardation occurs in the sampling pipe, the distortion of flow around the entrance end of the pipe causes an undue proportion of dust to lodge in the sampling pipe and be

velocity when working with gas of 1.5 grains, or more, of dust per cu. ft. There is undoubtedly an error made in sampling even cleaner gas at an incorrect velocity but probably not so great an error. There is so little known in regard to dust in gas during the various phases of its passage from the furnace to stoves, boilers and cleaners, that a mass of work must be done and many experiments be made before the influence of velocity of sampling can be definitely known with gas of various degrees of cleanliness.

To determine dust by the Velocity Method, if we may call it such, the following are the conditions which must be known and the means for arriving at the same.

1. *Dew Point of the Gas.*—This is obtained before starting the dust test by means of the special psychrometer shown in Fig. 1, which is really an aluminium casting of 2 $\frac{1}{2}$ inches diameter arranged for supporting a dry and wet bulb thermometer in a stream of gas flowing from the main into the atmosphere. By means of a gate valve the flow of gas through

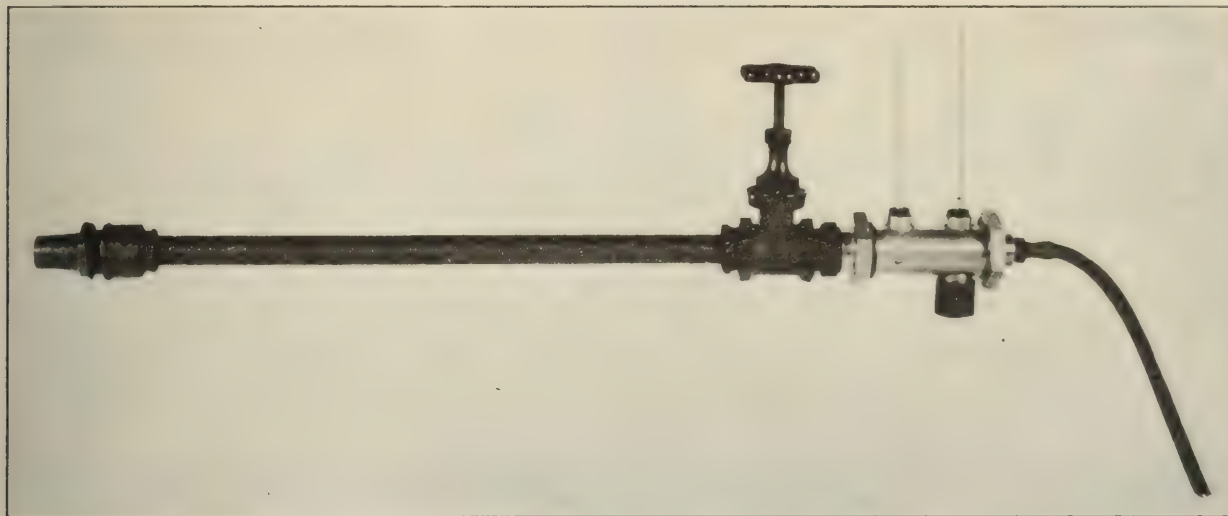


Fig. 1.—Special psychrometer used for determining the dew point of blast furnace gas

carried over into the filter. This is exactly as we would expect since, in a section of gas and dust mixture equal to the area of the sampling pipe, the dust, having greater inertia than the gas, would naturally be more difficult to distort, and instead of flowing around the open end of the sampling pipe would lodge inside of it and be carried over into the filter. On the other hand, if the flow of gas in the sampling pipe exceeds that in the main, there will be a flow of gas from a zone outside the section equal to the area of the sampling pipe, and an undue proportion of gas will be distorted from its path and drawn into the sampling pipe. Hence, in case of excessive velocity in sampling, low results may be expected. After the above experiments had been completed, both sets of apparatus were run at the same correct velocity of 43 to 45 feet per second, and in all cases the results checked very closely—within a few hundredths of a grain.

These tests settle once for all the question of sampling

the instrument is regulated so that the temperature of the gas is reduced to a point between 130° and 140° F. Dry and wet bulb readings are then taken for half an hour or more. By referring to Psychrometric Tables, the dew points are obtained and the average dew point for the period is accepted for use in the formula used in running the test. For gas from furnaces on Bessemer burden the average dew point is about 118° F.

2. *Weight of One Cubic Foot of the Gas at Main Conditions.*—From average analyses of the gas in question, the weight of one cu. ft. of dry gas at standard conditions of 62° F. and 30" Hg is calculated, using the following weights, as recently given by the Bureau of Standards, Washington, D. C.

CO ₂	0.11660 lb. per cu. ft.
CO	0.07375 lb. per cu. ft.
H ₂	0.005302 lb. per cu. ft.
CH ₄	0.04228 lb. per cu. ft.
N	0.07377 lb. per cu. ft.

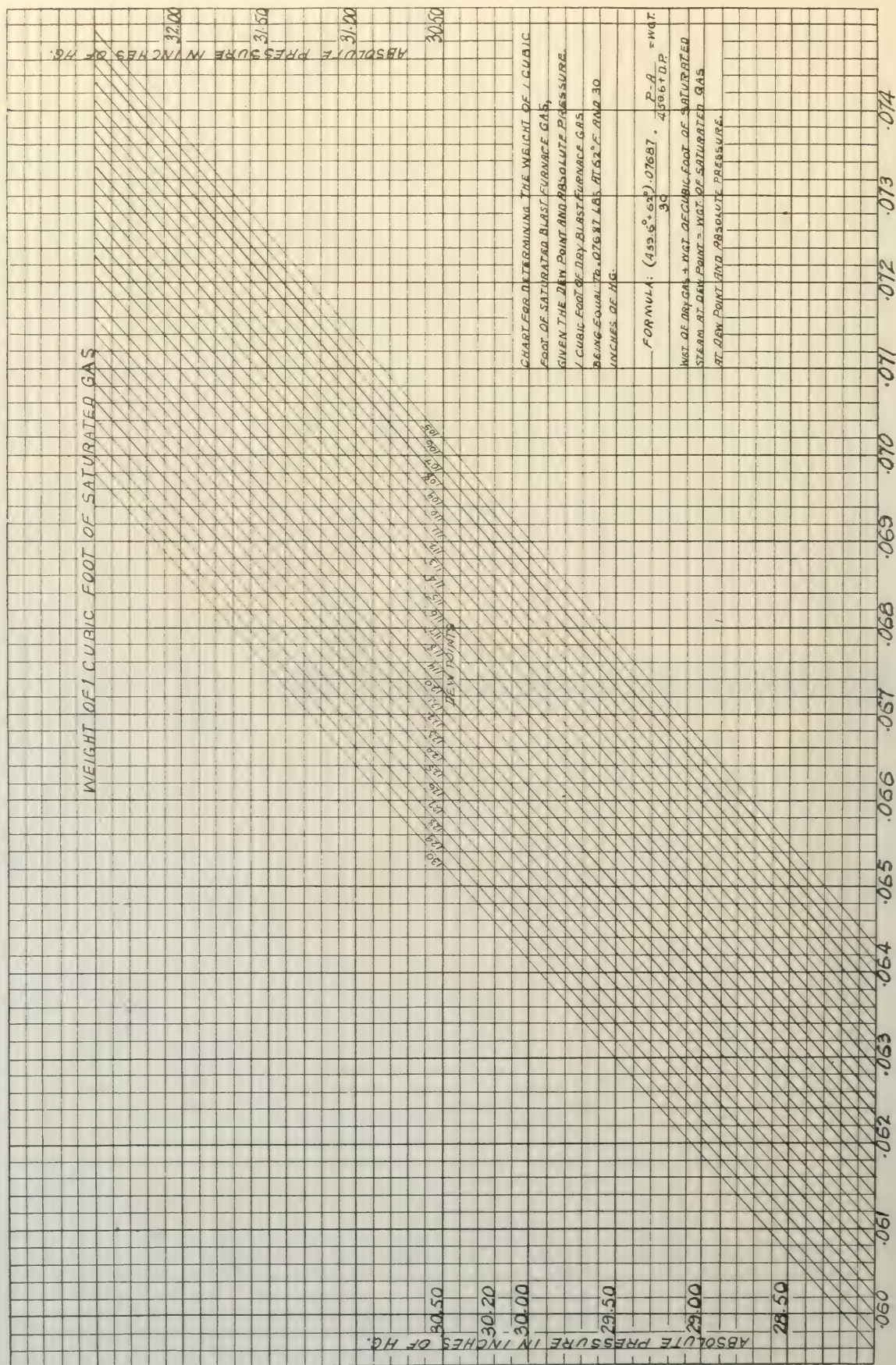


Fig. 2.—Chart for determining (y).

The average analysis, by volume, of blast-furnace gas from a furnace on Bessemer burden is as follows:

Cu.	13.6	by vol dry gas
CO	26.1	
H	3.5	
CH ₄	0.2	
N	57.2	

Thus one cu. ft. of blast-furnace gas at 62° F. and 30" Hg weighs 0.07687 pound. These figures are the average of the results of over 4000 daily analyses of 24-hour cumulative samples.

Knowing the absolute pressure of the gas at main conditions, and having determined the dew point, the weight of one cu. ft. of saturated gas at this dew point temperature is determined from the chart, shown in Fig. 2, which gives the combined weight of dry gas, calculated to the desired temperature and pressure, and the aqueous vapor, as given in Marks and Davis' Steam Tables, in one cu. ft. of

developed from the well known velocity formula $V = \sqrt{2gh}$ as follows:

If: V equals velocity, in feet per second.

g equals gravity, equals 32.16.

h equals height of a column of gas in question one foot square equal to the velocity head.

h' equals equivalent velocity head in inches of water.

p equals equivalent velocity head in lbs. per sq. ft.

d equals weight of one cu. ft. of the gas in question at main conditions.

$$\text{Then: } h = p/d \quad (1)$$

And since one cu. ft. of water weighs 62.3 pounds

$$p = h' \cdot 62.3/12 \quad (2)$$

$$V = \sqrt{64.32 \cdot h' \cdot 62.3/12} \quad (3)$$

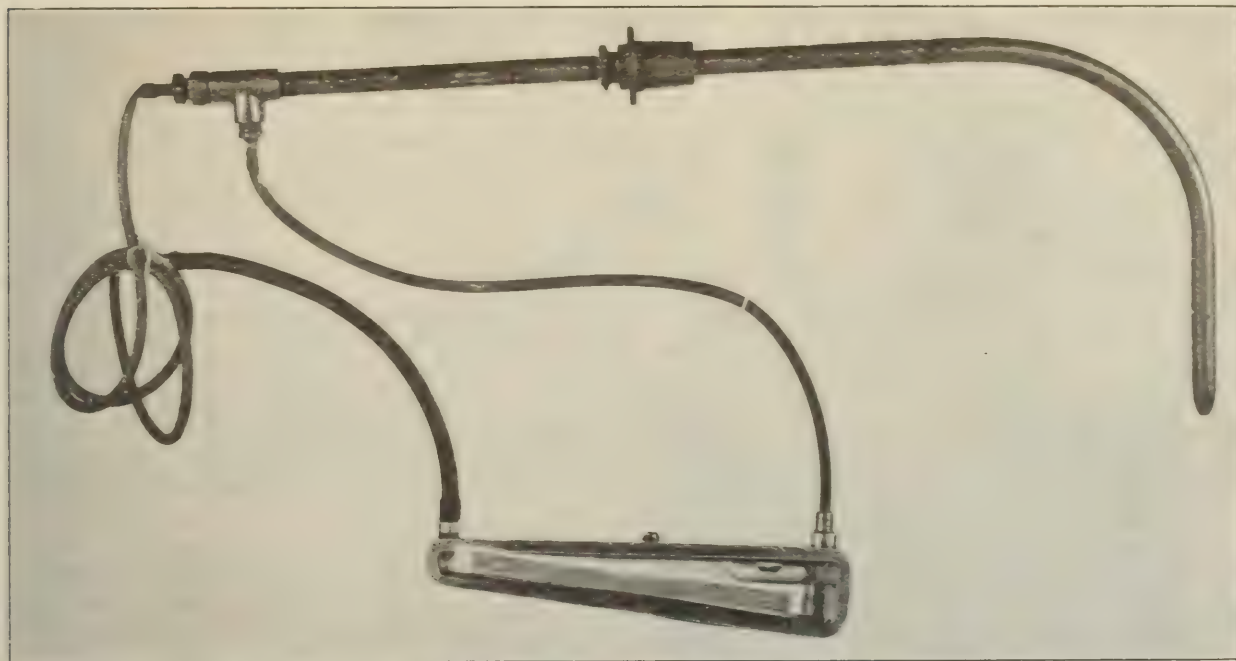


Fig. 3—Pitot tube connected with Ellison gage

saturated gas at any desired pressure and dew point. This figure is then converted to the new weight at the main temperature, calculating as though the saturated gas were a perfect gas.

3. *Temperature of the Gas in the Main.*—This is obtained by a mercury thermometer with an 18-inch stem, which is inserted into the main just beyond the point where the dust sample is taken.

4. *Pressure of the Gas in the Main.*—This is determined by means of a mercury column, graduated in inches.

5. *Velocity of the Gas in the Main.*—Knowing the weight of one cu. ft. of gas, at main conditions, all that is needed to determine velocity is the velocity head expressed in inches of water. This is obtained by a properly designed Pitot tube, shown in Fig. 3, and an Ellison differential gage. The formula is

$$V = \sqrt{\frac{33.4 h'}{d}} \quad (4)$$

6. *Temperature of the Gas at the Meter.*—This is obtained by means of an ordinary chemical mercury thermometer inserted at the proper place on the meter (see Fig. 4).

7. *Pressure of the Gas at the Meter.*—This is obtained by means of a mercury column attached to the meter (see Fig. 4).

8. *Time in Seconds Required to Meter 0.1 Cubic Foot at Meter Conditions.*—Ordinary wet test meters are so graduated that the large indicator makes one complete revolution for each 0.1 cu. ft. An ordinary stop watch, graduated in fifths of a second, is used to obtain the time required for the indicator to make one revolution.

9. *Aqueous Pressure at the Temperature of the Dew Point and of the Gas at the Meter.*—All aqueous pressures used are taken from "Steam Tables and Diagrams," by Marks and Davis.

10. *Total Grains of Dust Collected.*—The filter used is the Brady Gas Filter, shown in Fig. 5. In this apparatus the dust is collected in a Soxhlet extraction shell of 33 by 93 mm., supported in a horizontal

seconds time, makes this a convenient apparatus for dust determinations.

11. *Total Volume of Gas Metered.*—This is determined by a Junker's improved wet test meter graduated in cu. ft. The greatest speed at which this meter can correctly register is about 0.1 cu. ft. per 9 to 10 seconds. This fact must be borne in mind when selecting the size of the sampling pipe to be used to obtain the desired velocity.

12. *Duplication of Main Velocity in Sampling Pipe.*—Having described the requisites for a correct dust test and means for procuring the same, it will next be in order to briefly describe the method of obtaining the correct velocity in the sampling pipe—or in other words, of duplicating the main velocity. The method for obtaining the latter has already been given above. The Pitot tube mentioned, shown in Fig. 3, is inserted at the side of the sampling pipe and remains there permanently during the test. The velocity head, as shown by the Ellison gage, see Fig. 3, therefore, is constantly before the operator. The armoured 18-inch stem thermometer is also permanently inserted in the main beyond the sampling pipe, as explained before, and thus shows any changes of main temperature which may occur. In tests made on blast-furnace gas near the furnace, it will be found that the greatest variables to be dealt with are the velocity head and the temperature of the gas in the main. Of course, the other conditions also vary, but they are usually so slight that the velocity is not seriously affected. For testing purposes these latter variations may be neglected in our endeavor to maintain the correct sampling velocity during any one test, but not so with variations of temperature and velocity head. It therefore becomes necessary to make alterations in the rate of withdrawing our sample when changes in these two variables occur.

The expressions and calculations used in the mathematical computations for obtaining proper velocities are as follows:

V_m equals volume of gas at meter conditions metered in time t .

V_p equals equivalent volume of gas at main conditions.

V_1 equals equivalent volume of gas at dew point conditions.

T_1 equals absolute temperature of the dew point of the gas.

T_p equals absolute temperature of the gas in the main.

T_m equals absolute temperature of the gas at the meter.

P_p equals absolute pressure of the gas in the main.

P_m equals absolute pressure of the gas at the meter.

A_1 equals pressure of aqueous vapor at T_1 .

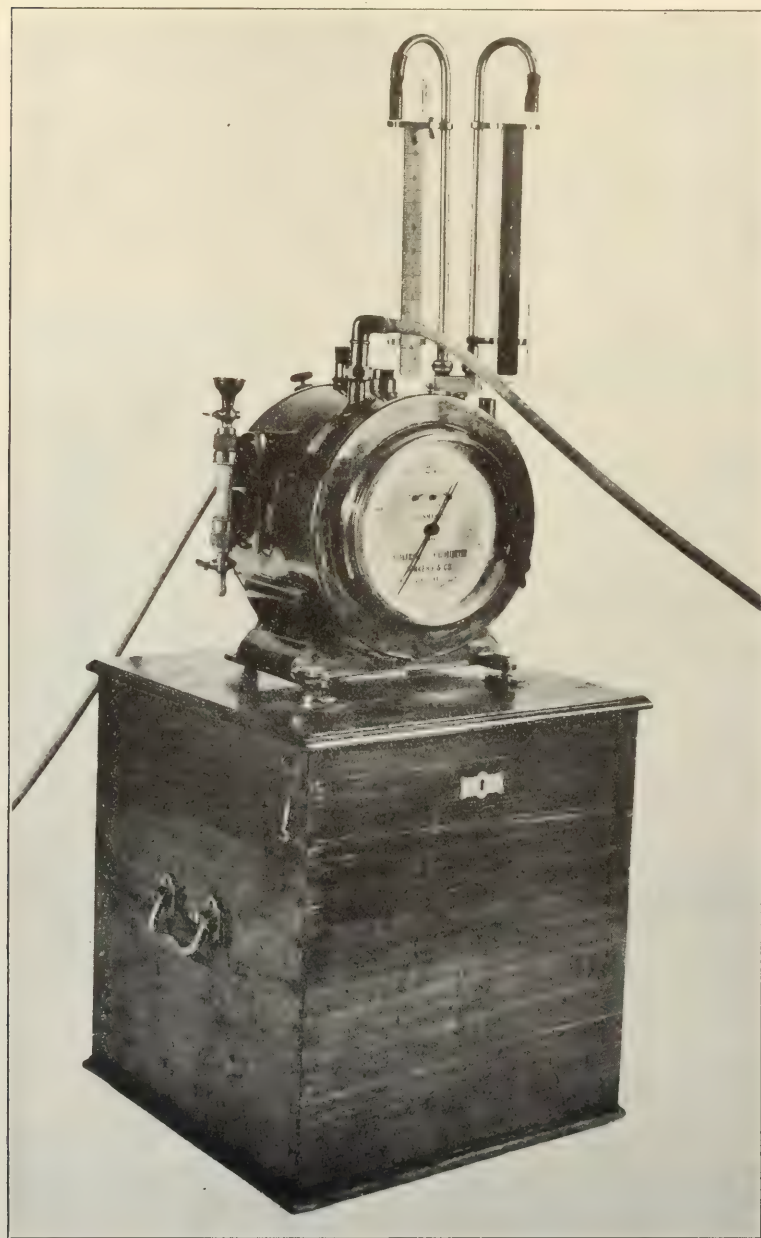


Fig. 4.—Wet test meter and attachments.

position by having its open end clamped between two tapering cylindrical faces. The gas flows through the paper shell into a surrounding metallic shell, there being a space of about $\frac{3}{16}$ of an inch between the outer surface of the former and the inner surface of the latter. The wonderful porosity of this filter and the convenience of being able to easily withdraw the used filter and substitute a new one in a few

A_m equals pressure of aqueous vapor at T_m .

t equals time in seconds required to meter V_m .

a equals cross sectional area of sampling pipe in sq. ft.

v_p equals velocity of gas in main in feet per second, therefore the velocity desired in the sampling pipe. Since the gas is cooled below its dew point before being delivered to the meter it will reach the latter in a saturated condition. We wish to determine what the volume V_m will be at actual main conditions in terms of V_m . This can best be shown in considering the operation in two steps: first, obtain the expression for the volume at dew point conditions; second, convert the volume at dew point conditions to actual main conditions. We know that in a cu. ft. of saturated gas the dry gas present will occupy the same volume as the saturated gas but the pressure will be different. We may, therefore, consider that V_m is the volume of either dry or saturated gas at the meter. Likewise, V_1 may be considered as being the equivalent volume of either dry gas or saturated gas at the

$$\frac{V_m}{a \cdot t} = \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_p}{T_m} \quad (9)$$

If the velocity in the main and in the sample pipe are to be equal then $V = v_p$.

Substituting the value of $V = \sqrt{\frac{334 h'}{d}}$ for v_p in formula (9), we have

$$t = \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_p}{T_m} \cdot \frac{V_m}{a \cdot \sqrt{\frac{334 h'}{d}}} \quad (10)$$

If we designate the weight of one cu. ft. of the saturated gas at the dew point and main pressure, as shown on the chart (see Fig. 2) as y , then

$$d = y \cdot \frac{T_1}{T_p} \quad (11)$$

Substituting this value of d in (10) we have

$$t = \frac{(P_m - A_m) \cdot V_m \cdot T_p}{(P_p - A_1) \cdot a \cdot T_m} \cdot \sqrt{\frac{y \cdot T_1}{334 \cdot h' \cdot T_p}} \quad (12)$$

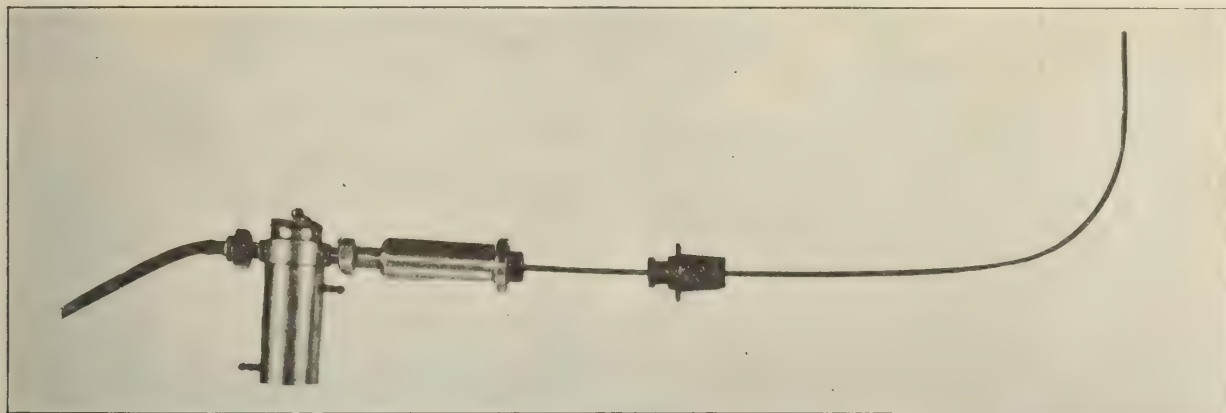


Fig. 5.—Sampling pipe, Brady filter and condenser.

dew point. Considering both volumes as being of dry gas, for the time being, we may apply the gas laws to convert V_m to V_1 , knowing the temperature T_m and T_1 and by subtracting the vapor pressures as given by the tables from the absolute pressures P_m and P_p .

$$V_1 = V_m \cdot \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_1}{T_m} \quad (5)$$

Having now the volume at the dew point we need only convert it to its new volume at T_p .

Thus we have

$$V_p = V_1 \cdot \frac{T_p}{T_1} = V_m \cdot \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_p}{T_m} \quad (6)$$

The volume V_p , being the volume of gas which flows through a in t seconds, then

$$V_p = v_p \cdot a \cdot t \quad (7)$$

From (6) and (7)

$$v_p \cdot a \cdot t = V_m \cdot \frac{P_m - A_m}{P_p - A_1} \cdot \frac{T_p}{T_m} \quad (8)$$

or

or

$$t = \sqrt{\frac{y \cdot T_1}{334}} \cdot \frac{V_m (P_m - A_m)}{T_m \cdot a \cdot (P_p - A_1)} \cdot \sqrt{\frac{T_p}{h'}} \quad (13)$$

This arrangement is most convenient, since for any test the above two factors on the right side of the equation may be considered as constant, and the third factor only will vary. This last factor is determined with the slide rule as often as changes in conditions warrant. The result of the latter calculation is then multiplied by the already obtained product of the first two factors. The final figure thus obtained will be the time in seconds which should elapse while the indicator on the meter is making one revolution, in order to insure the same velocity in the sampling pipe as in the main.

The actual method of running a dust test is as follows: Having selected the most advantageous point at which to withdraw the sample, four holes are drilled in the main in the following relative positions: The sample hole should be in such a position that the sampling pipe can be easily inserted and withdrawn

from the main at will, and should be tapped for a $1\frac{1}{2}$ -inch pipe thread. At about the same level, assuming that the main is vertical, another $1\frac{1}{2}$ -inch hole is tapped for the Pitot tube. Beyond these holes, relative to the flow of gas, a 1-inch hole is tapped for the large armoured thermometer, and several inches at one side of this 1-inch hole, a short length or nipple of $\frac{1}{8}$ -inch pipe is inserted to receive the rubber tube connecting with the mercury column which is used to show the static pressure of the gas. Brass collars, having an inner tapering surface, ground to fit similarly tapering plugs, are screwed in the $1\frac{1}{2}$ -inch holes. All parts of the apparatus inserted in the main at any time during the test are fitted

accurate readings with this apparatus, a velocity of at least 15 feet per second should be maintained while making dry and wet bulb readings. The Pitot tube is connected to an Ellison 2-inch differential draught gage by means of suitable tubing. In practice it is advisable to insert a three-way stopcock in each tube so that by turning both cocks simultaneously one-half turn, the gas pressure is shut off and each end of the gage subjected to atmospheric pressure only. The oil in the gage tube can then be made to register zero to start with. This also gives excellent means of checking up the gage at any time during the test. The main is then explored to find the zone of average velocity, and the sampling pipe is later

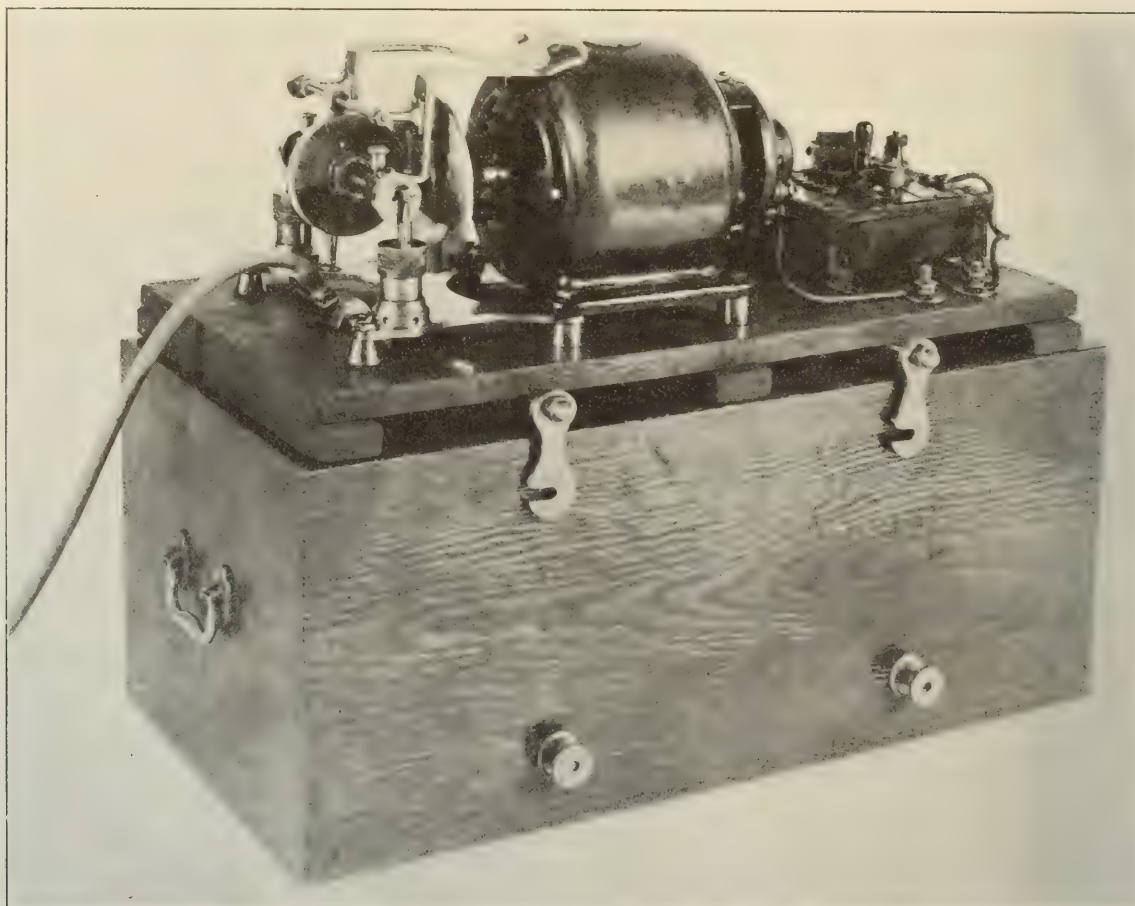


Fig. 6 —Suction pump connected to $\frac{1}{4}$ H. P. motor.

with the above-mentioned, tapering plugs which fit these collars and thus allow the insertion and withdrawal of such apparatus without making any threaded connections. A solid tapering stopper is used to plug the hole when there is no test being run. The special psychrometer is next inserted in one of these $1\frac{1}{2}$ -inch collars and the Pitot tube in the other.

It is sometimes necessary to insert a length of $1\frac{1}{2}$ -inch pipe between the tapering plug and the psychrometer to facilitate cooling the gas down to the proper temperature without too much loss of velocity. It may be here stated that to obtain

adjusted to sample at this same distance within the main. The armoured 18-inch stem thermometer is next screwed in place and connection is made by rubber tubing between the small $\frac{1}{8}$ -inch nipple and the mercury column on the meter used to register static pressure. Readings are then taken periodically for 30 minutes or more, of the velocity head, dry and wet bulb temperatures, main temperature, and static pressure. By means of the Psychrometric Tables the average dew point is determined from the dry and wet bulb readings. The average data obtained from all these readings can then be used to determine the average velocity in the main by use of

the velocity formula given above. Having determined the velocity at which the gas flows in the main, and, therefore, the velocity at which the gas must flow in the sampling pipe, we are now in a position to determine what size sampling pipe will be the most convenient to use. If the operator has had some experience, this can readily be decided from past experiments, but, if it is desired to mathematically determine the correct pipe to be used, equation (9) may be solved for a . By substituting atmospheric pressure and temperature for the meter conditions in the formula to determine t (see Formula 9), an approximate time for metering 0.1 cu. ft. is obtained. It must be understood, of course, that only an approximate figure is desired at first, since, as soon as the test starts, the necessary data will be obtained for calculating a more accurate result. In all of these calculations, a 10-inch slide rule is used and the result is accurate enough for the desired purpose.

A previously dried and weighed Soxhlet shell is next inserted in the Brady filter, which is then attached to the sampling pipe decided upon, and the aluminium condenser is connected to the exit end of the filter. A rubber tube of $3/8$ -inch diameter is used to connect the exit end of the condenser to the meter and another similar tube connects the exit end of the meter to the suction pump, shown in Fig. 6. In case the static pressure of the gas is sufficiently high it may be unnecessary to use the pump, in which case a screw cock placed on the tubing from the exit end of the meter serves to regulate the flow of gas through the sampling pipe. The apparatus being connected and ready for the test, an aluminium cap is slipped over the entrance end of the sampling pipe, the hole in the main is opened, and the pipe inserted in position, thus sealed, in order to warm up and prevent a deposition of moisture from tending to clog up the pipe on starting the test. At the same time the electric heater, which consists of a tin box containing two 16 c. p. electric bulbs, is placed in position surrounding the Brady filter and the reading of the meter is recorded. When both the sampling pipe and the filter have become heated, the apparatus is quickly withdrawn from the main, the aluminium cap promptly removed, and the pipe again inserted ready to take gas. As soon as possible after inserting the end of the sampling pipe in the main, the operator throws the switch which starts the pump, causing the sample to be drawn through the apparatus. By means of a wire suspended from above, or a stick supported on the floor, the apparatus is braced to keep it in a horizontal position. The operator at once begins to record the various readings such as meter pressure and temperature, main pressure and temperature, velocity head, static pressure and time required to meter 0.1 cu. ft. With this data and the figures from the aqueous pressure table he is able to obtain the correct value for t by means of the formula given, which is already partly calculated as previously described. From now on, readings are recorded regularly at specified intervals and quick calculations continuously made with the

slide rule to insure running the test at the correct velocity. At the end of the test the sampling pipe is withdrawn, the filter shell removed and a new one inserted for the next test. The meter is read and the difference between this and the previous reading gives the volume of gas metered. The shell containing the dust is dried for one hour and again weighed in a weighing bottle. The difference between this weight and the weight of the empty shell gives the total weight of dust collected. The average velocity of the main for the entire period is carefully figured together with the average velocity through the sampling pipe, and results are not accepted if a variation of over 5 feet per second was obtained between the two. The pump used is a friction-driven suction pump attached to a $1/4$ h. p. motor, and by means of a knurled wheel the speed of the pump may be regulated at will to obtain the desired velocity of sampling. The period of ordinary tests varies from 30 minutes to one hour and the size of the sample taken varies from 10 to 25 cu. ft., figured to standard conditions of 62° F. and 30 inches Hg. The size of sampling pipe most suitable to ordinary blast-furnace conditions is $3/16$ -inch inside diameter.

If the proper sampling pipe has been chosen, apparently considerable variations in conditions have a very slight effect on the rate of correct metering. While the above description of manipulations may give the idea that the method of running the test is difficult and complicated, it must be borne in mind that it is impossible and entirely unnecessary to make such delicate adjustments that the velocity in the sampling pipe will exactly duplicate the main velocity. It has been proved by our tests that a velocity in the sampling pipe within two or three feet per second of the main velocity is all that is necessary. Again, with practice it is surprising how expert the operator will become in judging what change in speed of sampling, or running the pump, is necessary for given changes in conditions. He is able to adjust his speed by judgment and then check up with the slide rule with surprising success. In about 100 tests run under quite a range of blast-furnace conditions our records show that the average velocity of the gas through the sampling pipe is within one or two feet per second of the main velocity.

SUMMARY.

1. Dust tests made in a continuously flowing stream of gas, where the dust per cu. ft. runs higher than 1.5 grains, are valueless unless the gas has been withdrawn from the main within two or three feet per second of the main velocity. It is possible that this statement may also apply for gas where the dust per cu. ft. is less than 1.5 grains, especially if ultimate results are desired.

2. Where the velocity of the gas in the sampling pipe is less than the velocity of the main the results obtained are high. Conversely when the velocity of sampling is too great, low results are obtained.

3. In all cases where it is desired to determine dust in gas the sample should be withdrawn through

a sampling pipe curved with a radius of 12 inches and facing the flow of gas.

4. The sample must be withdrawn where possible from a vertical pipe, or as near vertical as practicable and the sampling pipe should be inserted to such a degree

that the open end is in that region of the main where the mean velocity has been found to exist.

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PLANTS AND MACHINERY

A NEW ACCELERATED TEST FOR PAINTS.

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The ease with which iron corrodes when subjected to the action of electrolysis suggested the experimental work undertaken for the purpose of developing an accelerated test for the efficiency of paint used on metallic surfaces. When iron is coated with a protective paint, no corrosion takes place as long as moisture and air can be excluded. Whatever the real mechanism of corrosion may be, it is recognized that a paint must protect the metal surface by insulating or excluding it from the activity of air and moisture. Any means, therefore, that may show the resistance of paint materials to the breaking down of the coating film may be used to measure the comparative value of such films with regard to their permanency or endurance under actual and less active conditions.

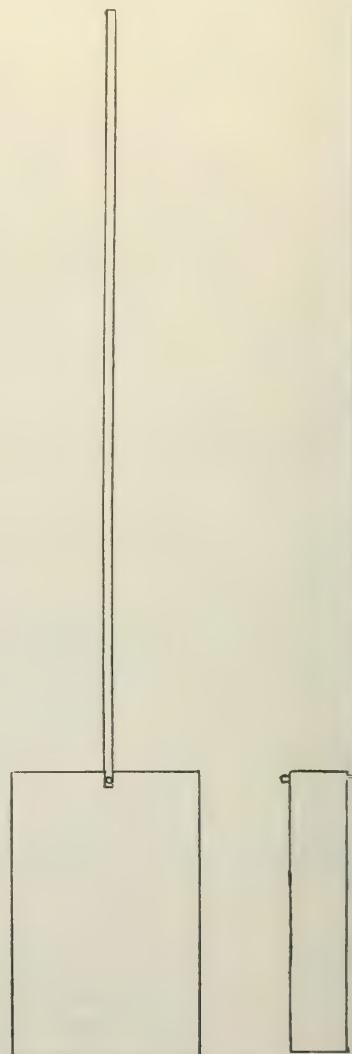
The apparatus used in obtaining the data given in the tables below consists of a simple electrolytic cell containing a normal salt solution for the electrolyte. The anode was a piece of clean steel coated with the paint to be tested. The cathode was platinum and the electrodes were placed four inches apart. Eight volts of direct current were used. A milliammeter was connected in the circuit to indicate the current flowing. Ammeter readings were taken as shown in Table III and from these readings and the constant voltage, the wattage was computed.

The painted electrodes used were made of pieces of steel about 1.4" long, 1.0" wide by 0.3" thick. A piece of copper wire about six inches long was fixed into one end of this steel rectangle by first cutting across the end with a hack saw a notch about an eighth of an inch deep and then wedging the wire into it. The diameter of the wire should be a little greater than the width of the saw kerf. The wire was then bent upwards as shown in the accompanying sketch.

The electrodes thus made were given two coats of paint, about a week being allowed for the first coat to dry. When the second coat was apparently dry, the electrodes were placed in an oven and kept at 45° C. for 12 hours. In order to facilitate rapid and uniform drying, it was found advantageous to round the edges of the electrode. (All the tests given in Table III except red lead (a) and aniline pitch dip were made with square cornered electrodes.) The electrodes were all of the same area and immersed in the solution to the same depth. The results are given in Table III.

For the purpose of this experiment, the insulating efficiency of the paints tested is taken as inversely

proportional to the wattage at the end of six hours. With a constant voltage, the efficiency is also inversely proportional to the average conductivity for the first six hours. While in general the experiments were conducted for 24 hours, in some cases the paints broke



*Sketch of Electrode.
Natural Scale*

down so completely before that time that the test was discontinued. For this and the additional reason that, in most cases, a nearly constant current had been reached by the end of six hours, that period was made the basis of comparison.

TABLE I.—PASSIVITY. BUBBLING TEST.

Pigment or base of	Weight. Steel Lost. Gram.	Pro- portional area of steel.	Wt. lost per unit area.	Relative inhibitive value.
1. Aluminum paint...	0.0562	0.938	0.0598	1.000
2. Tar cement paint...	0.0780	0.939	0.0832	0.718
3. Asphaltum paint...	0.1000	1.000	0.1000	0.598
4. Red lead...	0.1390	0.921	0.1510	0.396
5. Pitch paint...	0.203	1.032	0.1970	0.302
6. Acheson graphite...	0.222	0.912	0.2160	0.277
7. R. I. W. paint...	0.279	1.000	0.2790	0.214
8. P. & B. paint...	0.298	0.912	0.3270	0.185
9. Slate lacquer...	0.355	0.982	0.3650	0.169
10. Cement paint...	0.4441	0.904	0.491	0.122

TABLE II.—PASSIVITY. DAMP FILM TEST.

Order of efficiency.	Pigment or residue.
1.....	Red lead
2.....	P. & B. paint
3.....	Aluminum paint
4.....	Asphaltum paint
5.....	Tar and cement paint
6.....	Acheson graphite
7.....	Slate lacquer

other of an insulation type like the one above described, are necessary to determine the efficiency of a paint. By carefully standardizing these tests it should be possible to compute the value of a paint in relation to some commonly accepted unit.

By way of illustration, we may use red lead for one example and aniline pitch paint for the other. The problem is to ascertain the relative efficiency of these two paints. Let "I" equal the inhibitive value of a paint and "R" the resistant or insulating value of the same paint, then "V" the total value of the paint equals "RI." (An absolute standard to which to refer the inhibitive and insulating values of a paint must, of course, be eventually chosen.) In the case of red lead

$$V = 0.282 \times 0.396 = 0.112$$

and for aniline pitch paint

$$V = 0.473 \times 0.302 = 0.145.$$

TABLE III.—INSULATION TESTS.

Paint used.	No. of coats.	Voltage.	Amperage at end of						Wattage at end of						Efficiency P. I. W.	
			0 min.	10 min.	30 min.	1 hr.	2 hrs.	6 hrs.	24 hrs.	0 min.	30 min.	1 hr.	2 hrs.	6 hrs.		24 hrs.
1. R. I. W. paint.....	2	8.0	0.002	0.005	0.008	0.010	0.013	0.012	0.040	0.0006	0.0028	0.0073	0.0193	0.0693	0.5273	1.00
2. Pitch in aniline.....	2	8.0	0.002	0.005	0.010	0.015	0.020	0.040	0.040	0.0006	0.0031	0.0091	0.0266	0.1466	0.8666	0.473
3. Red lead (a).....	2	8.0	0.000	0.003	0.008	0.015	0.020	0.090	0.115	0.00025	0.0021	0.0081	0.0256	0.2456	2.095	0.282
4. Red lead (b).....	2	8.0	0.000	0.003	0.010	0.028	0.045	0.090	0.115	0.0002	0.0024	0.0115	0.0480	0.3180	2.168	0.218
5. Cement paint.....	3	8.0	0.025	0.032	0.042	0.054	0.065	0.070	0.060	0.0048	0.0171	0.0411	0.1056	0.3756	1.545	0.185
6. Acheson's graphite.....	2	8.0	0.055	0.058	0.066	0.075	0.088	0.100	0.100	0.0094	0.0300	0.0652	0.1467	0.5227	2.323	0.1315
7. P. & B. paint.....	2	8.0	0.020	0.100	..	0.130	0.130	0.130	..	0.005	..	0.101	0.231	0.751	..	0.0923
8. Asphaltum paint.....	2	8.0	0.025	0.100	0.15	0.120	0.130	0.140	..	0.0104	0.0463	0.1048	0.2298	0.7698	..	0.0900
9. White shellac.....	2	8.0	0.000	0.100	0.150	0.180	0.200	0.200	..	0.00	0.0500	0.1325	0.3225	1.1225	..	0.0615
10. Slate lacquer.....	2	8.0	0.010	0.120	0.155	0.180	0.210	0.210	0.195	0.0126	0.0584	0.1419	0.3369	1.1569	4.8019	0.060
11. Aluminum paint.....	2	8.0	0.085	0.155	0.185	0.0183	0.0749
12. Dull black var-lac.....	2	8.0	0.120	0.150	0.180	0.0225	0.0775
Pitch dip ¹	very thick	8.0	0.002	0.0025	0.0025	0.0020	0.0010	0.000	0.000	0.0002	0.0085	0.0095	0.0110	0.0130	0.0130	5.33

¹ Not comparable with others.

Efficiency = K/W_6 . Assuming efficiency of R. I. W. = 1. Then $K = 0.0693$.
Wattage at end of 6 hrs. = W_6 .

COMPARISON TESTS.

In order to obtain other means for comparison, the same paints were tested by the accelerated tests described by Cushman.¹ Table I gives numerical values from the bubbling test while Table II gives the relative efficiency of the paints as determined by the damp film test.

A number of the paints were tested by Magnusson² and Smith,³ in attempting to find means to prevent the corrosion of iron in concrete. While in these experiments, the conditions were different, the results in the main tend to confirm the same order of relative efficiency.

INTERPRETATION OF RESULTS.

To obtain a comparative rating, the efficiency of some one paint was taken at unity and all others calculated on that basis. It is the opinion of the writers that two accelerated tests, one of the inhibitive character described by Cushman³ and the

comparative results which are consistent with service tests of a limited character.

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A THERMOSTAT FOR MODERATE TEMPERATURES.

By A. M. BUSWELL AND RALPH H. MCKEE.

Received August 7, 1911.

The ordinary thermoregulator consisting of a mercury interrupter and relay, operated at low voltage, for turning on and off the heating system (electricity or gas), has given satisfaction. The other simpler type of thermoregulator, depending on the effect of temperature on a gas or a liquid, placed in a vessel whose only outlet is a J shaped tube filled with mercury and having platinum wires piercing each arm to serve as binding posts for the electrical connections, is, in the forms previously used,¹ for a short time fairly satisfactory where a range of several degrees is allowable. But when it is desired to keep an in-

¹ Bull. 35, Office of Public Roads, U. S. Department of Agriculture.

² A. I. E. E. Proceedings, 30, 939 (May, 1911).

³ Loc. cit.

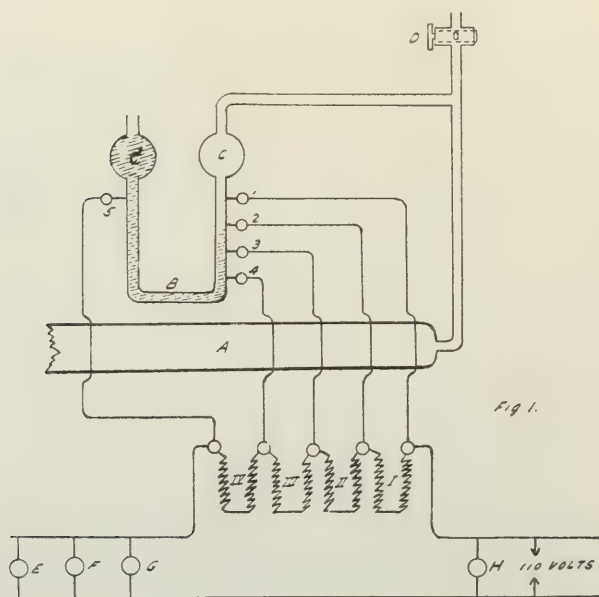
¹ Summerville, Elec. World, 57, 112 (1911); cf. bibliography given by Geer, J. Phys. Chem., 6, 101 (1902).

cubator constant to well within one degree the following difficulties arise.

1. When air is the expanding substance, the variation in atmospheric pressure, say 1.5 cm., will cause a change in volume of the gas of one in 50, whereas at 37° C., one degree will cause a variation of only one in 310; and the arcing, if the interrupter is used across a 110 volt circuit, volatilizes and oxidizes the mercury.

2. When toluene or ethyl alcohol is the expanding substance, the arcing cracks the liquid, giving carbon and a gas in the case of toluene and a permanent gas (hydrogen?) in the case of alcohol. The production of gas in either case is so great when 110 volts are used that the mercury is forced back and prevented from closing the circuit at the desired temperature.

The fact that there is a critical arcing voltage, varying with the composition of the electrodes, below which no arc can be formed, suggested that by cutting down the voltage across which the interrupter operated the production of gas might be eliminated. Experiment soon showed that with platinum and mercury electrodes operating across 20 volts or less, there was no arcing effect and practically no gas was formed by the spark at the make and break.



A thermostat (bacteria incubator) for water analysis, to be kept at 37° by a thermoregulator operated on this principle, was made, using a wooden box 14" × 18" × 24". Incandescent lights for heating were arranged at the bottom and a sheet iron plate was placed above them to give uniform distribution of heat and to shade the cultures.

The thermoregulator as shown in Fig 1 is easy of construction. A is a glass tube one centimeter in diameter, holding about 150 cc. of absolute alcohol. B is a capillary tube (inner diameter about 1.2 mm.) extending between the reservoirs C and C'. Mercury fills B and C'. A is connected to C and D by ordinary 6 mm. glass tubing. D is a stopcock for filling the apparatus. Nos. 1, 2, 3, 4 and 5 are platinum wires

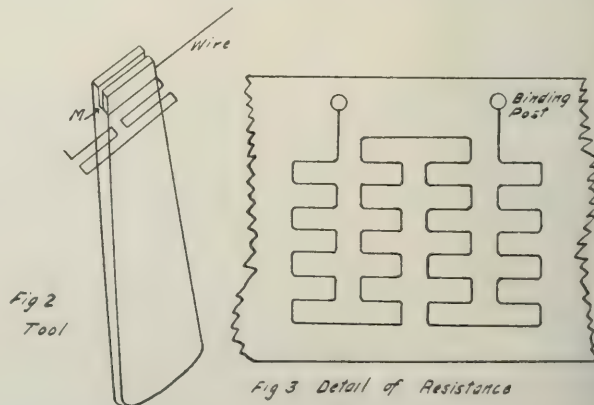
which pierce the capillary tube B and are connected by wires to the "Nichrome" resistances I, II, III and IV. The latter are mounted on an asbestos board placed with the lights beneath the iron plate, and are so constructed that the drop in pressure across each is 20 volts. Lights E, F and G (one 8 c. p. and two 4 c. p. lights) are arranged in series with the mercury, and with an eight candle power light H, connected to burn at full heat continuously, give somewhat more than enough heat to keep the temperature at 37° C.

The apparatus is so adjusted by the stopcock D that at 37° the mercury just makes contact with wire No. 2. The circuit then contains resistance I and the mercury in series with the lights E, F and G. If the temperature rises slightly the mercury is forced down, the contact at 2 is broken, and resistance II is thrown into the circuit. If it continues to rise, III and IV are thrown in in like manner. If the temperature drops, the mercury rises cutting out the resistances and brings the lights up to full heat.

Without attention the incubator kept within half a degree of 37° for two months. Reservoir C is large enough so that if the current is cut off for any reason, mercury will not be drawn over into A, and C' contains enough mercury so that under the same conditions the left arm of B will never be emptied below 5. On turning on the current the incubator comes up to temperature without attention.

The number of ohms for the resistances were determined by the formula $r = \frac{Rc}{L - c}$, where r is the resistance desired, R the resistance already in circuit, c the drop in voltage desired (20 volts in this case), and L the line voltage. In our case where the resistance of E, F and G was 110 ohms, resistance I was 24.4 ohms, II 29.9 ohms, III 37.0 ohms and IV 45.5 ohms. These resistances were made of No. 32 Nichrome wire, two ohms resistance per foot.

A convenient tool for making the resistance plates is shown in Fig. 2, in which M is a slit sawed in the



end through which the wire runs. The lower end is flattened so that the tool may be held easily between the thumb and fingers. It works equally well with ribbon or wire. The plates are as compact as those

of the same resistance wound in the old way on brads driven in a board, and not more than one-third the time is required for winding. The network may be conveniently stayed by the use of a little asbestos cement.

The glassblowing and bending is all of a simple character and can easily be done in three or four hours; and the winding of resistances and making connections should require no longer time.

UNIVERSITY OF MAINE,
ORONO.

[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF THE OKLAHOMA AGRICULTURAL EXPERIMENT STATION.]

A NEW FORM OF EXTRACTION APPARATUS.

By C. K. FRANCIS.

Received July 15, 1911.

The apparatus¹ (Fig. 1) consists of a modified condenser, A, and an improved flask, B, together with an extraction tube, C. There are no ground joints, the one seal necessary being made with mercury. No support is required for the flask.

The condenser used in the apparatus shown is of the Hopkins type, provided with a special extraction chamber, EC, and a dropping tube, DT.² The lower part of the extraction chamber is partially constricted on opposite sides about 10 mm. above the bottom. The two constrictions are so made (Fig. 2, IN) that each extends nearly one-half the circumference of the tube without meeting on either side. This arrangement leaves the internal diameter, 3 cm., unchanged in two diametrically opposite places and reduced to about 2.7 cm. for the remainder of the circumference.

The modifications of the Knorr flask are two knob-like perforated projections (Fig. 3, PP) on opposite sides of the neck and about 15 mm. above the base of the shoulder. These projections are so placed that they fit into the extraction chamber where the internal diameter is greatest. The holes (Fig. 3, HO) in the neck of the flask are about 3 mm. in diameter. These permit ample passage for vapor and return for the liquid which would otherwise collect around the neck of the flask.

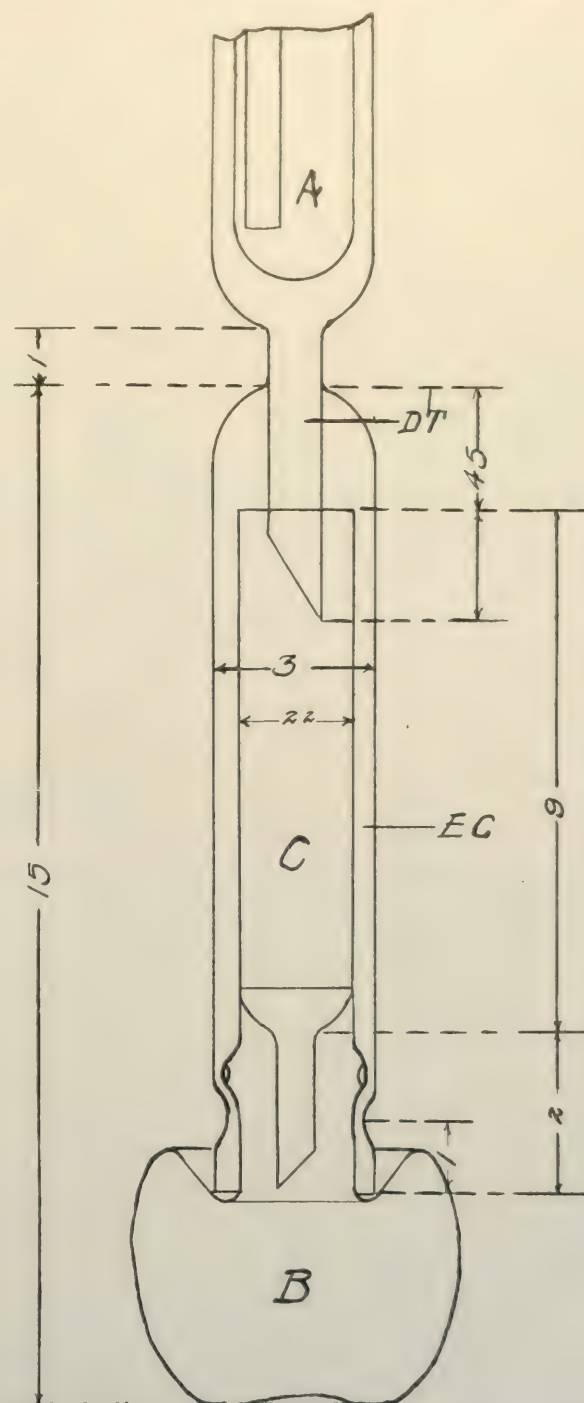
The extraction tube (Fig. 1, C) is 9 cm. long, 2.2 cm. external diameter and has a stem about 2 cm. long. It may be packed with cotton, asbestos, etc., together with the sample, and supported on the flask as shown in Fig. 1. A spiral spring of copper wire laid cross-wise and pushed down on the charge prevents the contents from being forced out of the tube by expansion of vapor. The regular paper shells may be used in place of glass tubes if supported on very small funnels.

The flask may be locked into the condenser by inserting the neck into the extraction chamber and giving the flask a quarter turn. This system fixes the flask securely and it cannot be accidentally pulled over or disturbed in any way. No support for the flask is necessary; this is especially convenient when heating with electricity or with warm water.

¹ A modification of a piece of apparatus designed by G. L. Holter and which has been in use in this laboratory for several years.

² Any of the ordinary condensers may be modified in the same way.

The temperature may be lowered by raising the apparatus above the source of heat. Electric lights, encased in compartments made of asbestos board, are used in this laboratory for heating the extraction flasks, but the apparatus described may be



Complete Apparatus.

Fig. 1.

found convenient where there is waste steam or warm water available.

The arrangement is economical in the use of solvents; 30 cc. of ether are ample for the usual fat extractions.

The position of the holes in the neck of the flask prevents any appreciable amount of condensed vapors

from collecting outside of the flask. The apparatus is especially applicable to alkaloidal and fat ex-

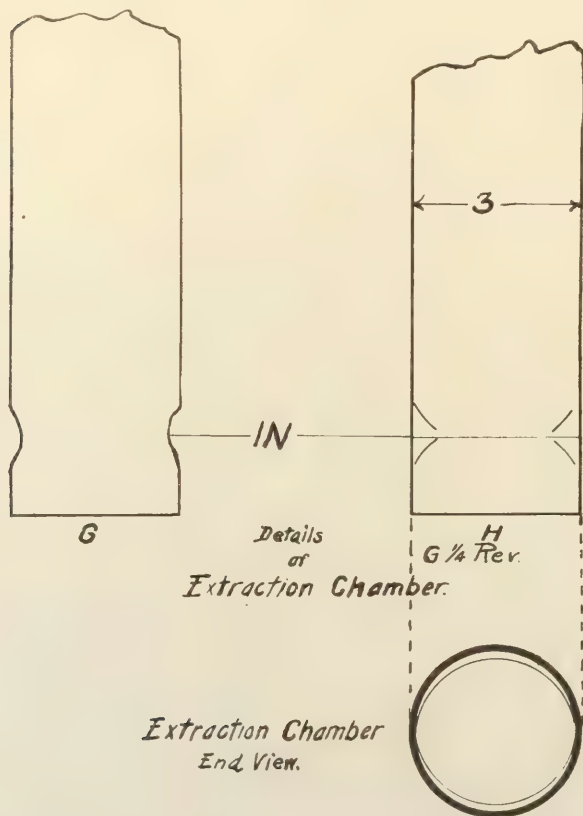


Fig. 2.

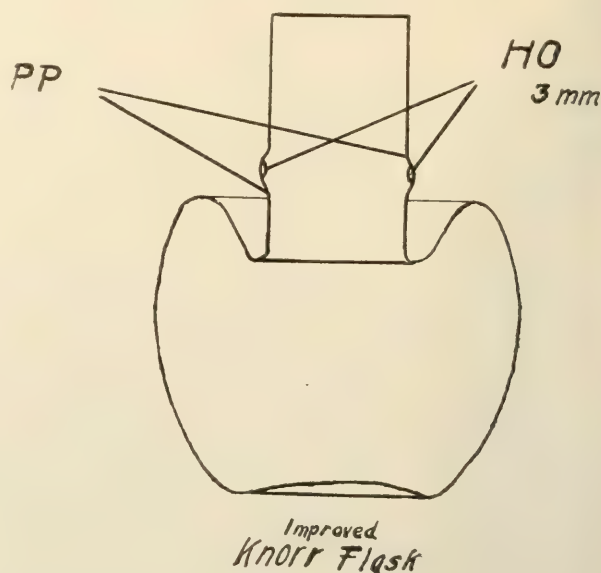


Fig. 3.

tractions. The cost is much less than that of the older forms of extraction apparatus.

E. H. Sargent & Co., Chicago, Ill., have recently made a large number of these special condensers and flasks for this laboratory.

STILLWATER, OKLA.

ADDRESSES.

THE CONSERVATION OF OUR METAL RESOURCES.¹

By ALBERT E. GREENE, Electro-Metallurgical Engineer, American Electric Smelting and Engineering Co., Chicago, Ill.

My theme before this congress is the conservation of our metal resources. Just as we are conserving the timber in the forests, utilizing the land we have heretofore called desert, using the exhaust steam of steam engines and greatly increasing their power, so also in the metallurgy of our base metals we are beginning to conserve a 0.1 per cent. of metal here and a 1 per cent. of metal there, which have hitherto gone to waste. Most of you are aware of the great progress made in recovering copper or silver or gold out of low-grade ores that only contain a very small percentage of these metals. Now in another field there is a loss which has been going on before our eyes with apparently no attention and it is a loss which amounts to millions of dollars per year. It is affecting not only large corporations but small producers even to a greater extent. The loss to which I refer is the loss of metal in the processes of making steel and other metals from ores.

In the production of the 20 million tons of steel per annum in this country there is a loss of metal by oxidation during the conversion process which proba-

bly aggregates one million tons. Most of this metal is lost in the slag and some of it can be reduced again by smelting the slag in the blast furnace, but in the Bessemer process a large part is blown out of the vessel in fine dust which is difficult to collect. The loss of metal by oxidation in the Bessemer process alone probably aggregates over 500,000 tons per year.

Another significant fact is that a very considerable part of the metal lost by oxidation consists of elements which are more valuable than iron—such as manganese and silicon. Those elements are usually required by specification in the finished steel, and although the iron ore usually contains enough of them, and the blast-furnace process usually reduces them into the iron in sufficient quantity to meet specifications without any additions, yet in the Bessemer and open-hearth processes they are almost invariably oxidized again and practically lost. When one remembers these facts and what it costs to reduce these metals into the iron and that after they are oxidized out they have to be replaced by expensive alloy additions to the steel, it seems as though this were an excellent opportunity to apply conservation theories to advantage.

My object in this paper is to point out how such losses as these can be and are beginning to be dimin-

¹ Presented before the Congress of Technology at the Massachusetts Institute of Technology, Boston, April, 1911.

ished, and another object is to show how the application of physical and chemical principles to those problems is one of the greatest aids we have in accomplishing this end. If I can do this I shall feel that, in some small way at least, I shall have served my Alma Mater, to whom I feel very greatly indebted.

It has been my privilege to have followed one of the newer fields of development influencing the conservation of our metal. This is the field of high-temperature chemistry which the advent of the electric furnace has opened up. It has been said by prominent steel men that in the next ten years the greatest developments in that industry will be those affecting increased metallurgical efficiency. I venture to say that in this one industry by the application of electricity together with improved chemical processes there will result a saving of metal which will amount to hundreds of thousands of tons per annum.

I wish to try to show how the electric furnace can influence conservation in such a way. It is not simply because the electric furnace provides a means of getting extremely high temperature but rather because by means of electrically developed heat we can simultaneously control the temperature and the chemical reactions wholly independently of one another. This is a most important fact and it opens up a whole new field of chemistry especially where the gaseous treatment of metal is involved.

For sake of comparison, let us consider the methods of heating now in use. Almost invariably heat is obtained by the combustion of fuel. The fuel is usually burned in the same chamber with the material heated so that gaseous products of combustion come in contact with the material. These products of combustion are themselves of an oxidizing nature since they always contain oxygen and, furthermore, to obtain high temperatures efficiently, it is necessary to burn the fuel with excess of oxygen which makes the atmosphere still more oxidizing. Thus we see that as a general thing high temperatures are obtained only under more or less oxidizing conditions, whether such conditions be desired or not. For example, where steel scrap is melted in an open-hearth furnace the steel takes up more or less oxygen in some form or other and the melted steel must be deoxidized by use of silicon and aluminum or other agents. Here much metal could be saved if the atmosphere could be controlled. In another example, such as the open-hearth process, where pig iron is being converted into steel, the oxidizing atmosphere aids in oxidizing the carbon, but the trouble is that it oxidizes the metal too, and this is the important cause of the great loss of metal referred to above. Even though the atmosphere may be modified slightly by allowing the gas to enter the furnace chamber next the charge and beneath the air, yet this does not prevent the loss by oxidation. And so we are practically driven to use the electric furnace if we desire to control temperature and atmosphere independently of one another.

Let us now see what can be accomplished by means of such independent control of temperature and gases

and let us consider in this connection the meaning and use of the term "neutral atmosphere."

One often hears of maintaining a neutral or a non-oxidizing atmosphere in an electric furnace to prevent oxidation. If we have a bath of steel and an iron oxide and lime slag on top of it, a neutral or non-oxidizing atmosphere would not necessarily prevent oxidation of elements in the steel. A neutral atmosphere would be in equilibrium with iron and an oxide of iron. If we are going to make use of the atmosphere to prevent oxidation it must be controlled and not kept simply neutral. It ought to be reducing in certain cases and oxidizing in others. And this leads me to the consideration of an idea whose application in practical processes I believe is new. It is this: We can, by controlling the temperature and also the composition of the atmosphere acting on a charge at a given temperature, effect a reduction of one substance and an oxidation of another substance at the same time by the same atmosphere. As far as I am aware, the application of this idea to the oxidation of an impurity out of a metal without oxidation of the metal itself and even with the reduction of the metal oxides is new. Its application to the conversion of iron into steel makes it possible to oxidize the carbon without the very great loss of metal I have already referred to.

Inasmuch as I was led to a clearer conception of such a process as this by a careful study of the chemical principles involved, it may be of interest to apply one or two of these principles to a simple case, for it is the application of these principles which I believe is of great value in improving the efficiency of such processes.

Suppose we are working with pig iron and can react on it in a furnace chamber with an oxidizing or reducing gas or mixtures of those gases and at any temperature and pressure. The physical conditions to be controlled in such a case are the temperature and the pressure of gas in the furnace chamber; the chemical conditions are the reactions between the different elements and compounds present.

The two laws particularly applicable in this case are the mass action law and the phase rule. Let us choose a simple reaction which might take place in the above example. The CO_2 gas present may act on the iron as follows:



The law of mass action tells us that if such a reaction goes on in a closed vessel at a given elevated temperature and pressure, a condition of equilibrium will be reached and the CO produced will bear a certain relation to the CO_2 present. For the given temperature and pressure the ratio of the amount of CO and CO_2 will have a particular value. The mass action law also tells us that if we force more CO_2 into the closed vessel the oxidation will proceed further, and if CO is forced into the space the oxidized iron will be reduced.

Now suppose we replace the mixture in the vessel by a mixture of CO and CO_2 , in which the CO is in

excess of the amount present under the equilibrium conditions just referred to; the result will be that some iron oxide will be reduced and CO_2 formed, and equilibrium will tend to be restored but the amount of solid or liquid iron oxide remaining will be less than at the start. We can make this replacement continuous, so that the gas in the chamber is always reducing toward iron oxide and we therefore have a means of carrying the reduction of iron oxide to completion and preventing the further oxidation of iron, it being remembered that the amount of solid FeO present does not influence the equilibrium. And, furthermore, this can be done with a gas containing the oxidizing agent CO_2 . By keeping enough CO_2 present it is possible to oxidize carbon without oxidizing iron, since carbon oxidizes more easily than iron at high temperatures.

With respect to temperature and what the control of it enables us to do, the phase rule tells us among other things what the effect of temperature will be on the equilibrium we have just considered. It tells us that the tendency of oxygen to separate from iron oxide has a certain definite value for every temperature. Increasing the temperature increases the tendency to separate or dissociate. This tendency is called the dissociation pressure of oxygen for the particular oxide and it has been measured for a few compounds. For our purposes, at present at least, we can and must get along without knowing what these actual pressures are, because they have not, except in a few cases, been determined; it serves our purpose, however, if we know what ratios of reducing gas to oxidizing gas will prevent the undesired oxidation for given temperatures. Thus we need only to know, first, what ratio for CO is needed with a given per cent. of CO_2 in a gas in order to prevent oxidation of iron at a given temperature, and second, how this ratio changes with the temperature.

The phase rule tells us the same thing about other elements, for example silicon, manganese, carbon, phosphorus, etc., these being the ones with which we are concerned in steel processes, and we find that at a given temperature these different elements as a rule have different tendencies to oxidize. Since the temperature affects different elements differently, we find also that at certain temperatures two elements may have the same tendency to oxidize, and the so-called critical temperature of the Bessemer process when both silicon and carbon have an equal tendency to oxidize is one of these temperature points.

To sum up a few of these considerations, we have seen how, by continuously controlling the atmosphere acting on a given charge, we may carry out any particular reaction to completion or how we may prevent a given reaction for an indefinite time; how an atmosphere which is reducing to one metal at a given temperature may not be reducing, but may even be oxidizing to another element, and that the term "neutral" is indefinite unless something more is specified.

And, finally, I think you will see how the electric furnace, by reason of enabling us to control temperature and, at the same time, oxidize one element while

keeping another reduced, makes it possible to do what the present steel-making processes cannot do, that is, oxidize carbon without the tremendous loss of other elements I have already referred to. It enables us to oxidize carbon and not iron or manganese or silicon; it enables us to oxidize phosphorus without oxidizing iron or manganese; it enables us to separate iron from copper by oxidizing the iron without oxidizing the copper; and these are only a few of the things that the combination makes possible.

The important question is: Can such processes be carried out economically, can they compete with present processes? When we started to develop these processes we had first worked them out theoretically, and we too wondered if they would really work in practice. We carried out an extensive series of tests on a small scale, and as these tests proved that it was possible to accomplish the oxidation of one element without oxidizing others, we then designed and built larger furnaces to try this process on a practical scale. Our first practical furnace was of about 300 pounds capacity for making steel for castings. I have presented a paper before the American Electrochemical Society at New York, which goes into more detail in regard to this process, but it may be of interest to make a brief comparison with the converter process used by many small steel foundries for making high-grade steel.

In the converter process, molten low-phosphorus pig iron is poured into the converter and blown with a blast of air usually through tuyeres near the level of the metal, the air burning out the silicon, manganese, carbon and considerable iron. In those small converters, such as used in steel foundries, the loss is very high; it is often more than 18 per cent. of the weight of the molten pig iron started with. True, about 4 per cent., which goes to make up that 18 per cent., is carbon and silicon, which have to come out any way, but there remains a loss of 13 or more per cent. which is so much waste of metal. In a plant making only 20 tons of molten steel per day, the value of this 13 per cent. of steel (for it would be steel if saved) would at \$30.00 per ton amount to over \$2300.00 per year, and in this loss is included manganese and silicon, which have to be put back again by adding alloys, and their addition entails further losses. These alloys, usually ferro-manganese and ferro-silicon, serve two purposes: they partly combine with the oxides in the iron which have come from the air blown through the iron and separate out as slag, and part of them remains in the steel and raises the percentage of these elements enough to meet the specifications.

The process we have developed and which we are calling an electric converter process is carried out in an electric furnace instead of a Bessemer converter, and the molten metal is blown with gas of regulated composition instead of with air. The vessel must be electrically heated because the reactions of the gas on the metal do not supply much heat, as the corresponding reactions in the Bessemer process do. We use a gas which may be obtained from a cupola, or a gas producer, or from a blast furnace. This gas would

contain 6 or 8 per cent. of carbon monoxide, CO, and 12 or 15 per cent. of carbon dioxide, CO₂. When blown into molten pig iron this gas does not oxidize iron or manganese, and as pig iron usually contains manganese in sufficient quantity to meet specifications, this process avoids replacing that element by expensive alloy additions. The metal is heated to about 1450° Centigrade and blown with this gas, and the carbon is taken out by it. The carbon is oxidized, but not the iron nor the manganese. There is a small loss of manganese by vaporization, but this is so small that after the carbon is out the percentage of manganese may even be larger than at the start.

In the small furnace which we have used to make various grades of steel, we have been able to convert pig iron into steel with a total conversion loss of only about 2.5 per cent. plus the weight of carbon burned, including metal spilled in handling and left in the furnace, and this compares with a total loss of 15 per cent. plus the carbon burned by the Bessemer process in small converters. This furnace was heated by induced electric currents in the metal. The process is now installed and under test in a two-ton furnace, and we believe that the developments we have made are a step toward the saving of that immense loss which is going on to-day.

One of the most interesting applications of the process has been in the production of manganese steel. As is well known, manganese steel containing about 12 per cent. manganese has very valuable properties of strength and resistance to wear, which render it very useful for such articles as railway crossings, rails, crusher-jaws, safes and many similar things. The scrap steel, such as heads and gates, etc., from castings made of manganese steel, contains a valuable amount of manganese, but in the melting up of manganese steel scrap in cupolas much of the manganese is lost and when the melted mixture of scrap and iron is blown in the converter, all the rest of the manganese not already lost is oxidized. This tendency of manganese to oxidize has made it practically impossible, at least from a commercial standpoint, to make low-carbon manganese steel, and the properties of such steel are almost unknown. By applying our process it has proved practical to melt manganese steel scrap into pig iron and then remove the carbon without practically any loss of manganese, and it has further proved practical to produce very low-carbon manganese steel in this way. The commercial saving resulting from the utilization of the manganese that has heretofore gone to waste is a most important consideration to the manufacturer, and this saving can be accomplished at a cost very much less than the value of the metal saved.

These examples of losses in steel processes are characteristic of similar losses in the metallurgy of various other metals; in the process of converting copper matte for removing the sulphur and the iron from the copper there is an oxidation of copper which totals up very high. Likewise in the metallurgy of lead there is a similar loss and in the case of many other metals. These losses can be prevented by the

use of electric heat for controlling temperature and simultaneously controlling the composition of the gaseous reagents.

The commercial practicability of such processes depends on many factors, but we believe that the losses which can be prevented will in a great many cases prove to much more than offset the cost of electric heating.

The field of chemistry opened by the electric furnace is a most fertile one from the standpoint of scientific research as well as on the practical side. We need exact knowledge about all the metals and elements concerned in high temperature metallurgy, such as the dissociation pressures of various metallic oxides and the variation of these pressures with the temperature. Such data will be of the greatest value to the manufacturer, so that there shall be an additional incentive to its collection of scientific workers. By means of such data and by the application of simple physical and chemical principles in practical processes I believe the chemist has in his power one of the greatest means to-day of aiding the cause of conservation of our metals.

THE WORK OF ENGINEERS IN THE GAS INDUSTRIES.

By FREDERICK P. ROYCE.

Received April 26, 1911.

The business of manufacturing and distributing gas is older than that of any other of the public utilities with the exception of that of distributing water.

Early in the nineteenth century companies were established and in active operation in England. Many of the companies still doing business in this country were organized and in operation prior to 1850. It was not until a much later date, however, that results due to the efforts of scientifically trained men were generally apparent.

The first dry distillation of coal producing gas for commercial purposes was accomplished in retorts made of iron placed in a horizontal position, the heat necessary being directly applied by furnaces placed underneath the retorts.

With the exception of the substitution in the retort of fire-brick material for cast iron, this type of retort, with slight modification, was used for many years and in some small plants is used to-day.

In the early days of the industry it was found that with little effort sufficient gas could be produced and sold at a high price for lighting purposes to furnish a satisfactory return on the capital invested.

At the time, little or no consideration had been given to the relations of the companies and the public, which are now properly regarded as of great importance.

It was not understood that to get the best results for all, these companies should be operated as regulated monopolies, and the earnings of the companies were not sufficiently large to invite general competition.

These gas companies then furnished all illumination not produced by lamps or candles.

Under such circumstances there was apparently

little incentive to the engineer to enter the business and apply a scientific knowledge to the reduction of the cost of the plant or of operating it.

As time went on these conditions changed, and in the early eighties a very strong competition was introduced through the development of the electric lighting companies, which for a time threatened to destroy the business of the gas companies and in some places actually did reduce it materially.

It was then absolutely necessary that the owners of these properties should devise means of reducing their operating cost and to do a much larger business at a smaller rate of profit.

This could only be done through the employment of trained engineers.

At that time coal gas was made almost exclusively and the largest element of cost in the production of the gas was in the carbonization of the coal. There has always been a saying to the effect that money was made or lost in the retort house, and it has been in the retort house that the greatest improvement has been effected.

As has been said, the retorts were then of the direct-fired type: the coal to be carbonized was placed in the retorts by hand and the coke was removed in the same way.

It was then considered good practice if 30,000 feet of gas could be made in a day by each man employed in the retort house. This hand-firing was slow, resulting in a serious waste of gas and loss of heat.

The first step toward improvement was the introduction of machinery to charge the retorts and remove the coke.

Notwithstanding the extremely difficult conditions under which this apparatus must be operated, it has been on the whole very successful. Numerous types of machinery have been built applicable to the smallest or the largest works.

At about the same time the regenerative setting of retort benches was designed and put in successful use.

In this a generator is made a part of the bench setting and used to produce carbon monoxide gas through partial combustion, using a limited amount of primary air. This monoxide gas is distributed as desired through the bench and brought in contact with secondary air which has been preheated by passing through flues adjacent to other flues through which the products of combustion are carried to the chimney. The carbon monoxide being fired as it combines with the secondary air produces a high heat which can be satisfactorily controlled, assuring a uniform temperature throughout the various retorts of the setting.

This type of bench was followed by the inclined retort setting. In this bench the retorts are set at an angle of approximately 31° from the horizontal, the charge being introduced from the top and distributed through the retort by gravity, the coke falling from the bottom mouthpiece as desired.

The principal advantage of this type of setting is in the avoidance of the use of expensive charging and drawing machinery.

The inclined setting was followed in a few years by the vertical type.

It is interesting to note that although experiments were made with vertical retorts in the very early days of the gas industry, it was not until three or four years ago that engineers in Germany were able to build and operate them successfully on a commercial scale.

The first successful installations of this sort were designed for intermittent charging and discharging. Little machinery was required to operate them and, due to the fact that the retort was completely filled with coal, a marked improvement was noted in the character of the by-products.

As the weight of the coal in the vertical retorts is supported principally by the lower mouthpiece rather than the retort itself, the mouthpiece being easily repaired as needed, there should be and apparently is an improvement in the life of the setting.

A more recent development in the vertical retort setting has been accomplished by the perfecting of charging and discharging apparatus, by means of which a continuous carbonization of the coal is effected.

A still further improvement in the carbonization of coal in large plants has been effected by the successful design and operation of the so-called coking chamber. This in reality is a development of the inclined retort, but instead of using a comparatively small retort which would contain a charge probably not to exceed one thousand pounds in weight, a large chamber designed to contain and carbonize six or seven tons is used. The bottom of this chamber is built at an angle similar to that of the inclined retort so that the coke slides freely from it when the mouthpiece, which is really the entire lower end of the chamber, is removed.

Through these developments the cost of labor has been greatly reduced, and whereas with the early benches there was a production of 30,000 cubic feet per man per day, with the coking chambers a production of 150,000 cubic feet per man has been made possible.

At the same time the yield of gas from a pound of coal measured by the product of its volume and candle power has been increased twenty-five per cent.

The amount of fuel required to carbonize the coal, an important item of cost, has been very greatly reduced.

The capacity of unit has been increased to such an extent that much less space is required to produce a given amount of gas, which results in a reduction of plant cost.

The quantity of certain by-products has been increased and the character of these by-products much improved. This has been particularly noteworthy in connection with the vertical type of setting.

The coke made in the vertical retorts and in the coking chambers is of much the same character as that made in the beehive oven. It is stronger and consequently a smaller percentage of it is in the comparatively worthless form of screenings or breeze.

A larger percentage of ammonia is recovered. The tar produced is better and comparatively free from lampblack and other impurities.

It is regrettable that most of the improvements noted in retort house operation have been due to the efforts of foreign engineers. The charging and drawing machinery was first perfected in England. The inclined and vertical retort benches for intermittent carbonization were developed by German engineers, and the continuous system of carbonization with vertical retorts is due principally to the efforts of Englishmen.

To American engineers, however, there may be fairly attributed the development of the water-gas process.

The Lowe type of apparatus developed in this country is now the standard throughout the world where water gas is made. It is estimated that more than one-half of the total production in this country is of water gas.

This has been of great importance in connection with the production of coal gas.

The cost of the latter is directly dependent on the price received for residuals, and it is probable that if coal gas only were made in this country the increased supply of residuals would be in excess of the demand, so that the average price received for them would be reduced and consequently the cost of producing the coal gas would be increased.

It is now common practice in America to make both water gas and coal gas in the same works. The water gas can be made of any desired candle power and mixed with the coal gas, making it possible to furnish a commercial product of almost any quality desired.

The improvements in the art, however, have not been confined to the generating house.

The quality of the gas depends in great measure on the method used to clean and purify it. The importance of this may be seen when it is realized that the so-called impurities in the gas, which are harmful as a part of the gas, are themselves valuable by-products when removed.

To obtain the best results the temperature of the gas must be made to pass through wide ranges during the different steps of cleansing and purification. Engineers have determined the correct temperature for each stage and have devised apparatus by which these conditions can be controlled.

This work of the engineers has produced a great decrease in the cost of gas. Twenty years ago it was possible to reduce the price of gas to a point where it could be made to compete successfully with

coal and other fuels, thus greatly increasing the market for it and definitely establishing the stability of the industry.

Some companies which sold gas at as high a rate as \$4.00 per 1,000 cubic feet in 1870 are to-day able to produce and sell it at less than \$1.00 per 1,000 cubic feet and still make a fair return on the necessary investment. This great decrease is the result of the reduced cost of production and of the largely increased output that followed it.

Through the development of the Welsbach mantle it is now possible to get much more light with a given amount of gas than could ever be obtained with the open burner and at the same time to use gas of a low candle power, thus materially reducing its cost. This has helped to place the gas companies in a position where they can successfully compete with the electric companies for a large portion of the lighting business.

The field at the present time is a most excellent one for the engineer. There are still opportunities to improve the methods of carbonization of coal and the generation of water gas. The highest efficiencies in these departments have been by no means reached. The actual chemical reactions in the process of carbonization and the effect on them of various temperatures offers a subject for further profitable study.

There is opportunity to increase the quantity of residuals recovered and to improve their quality. There is also every reason to believe that the market for these residuals can be substantially increased.

A small percentage of saving in the cost of the product is quickly reflected in the year's earnings. A company selling 500,000,000 cubic feet per annum is one of medium size, and yet a reduction of one cent per 1,000 cubic feet in the cost of manufacture or of distributing the gas means a saving to that company of \$5,000.00 per annum.

It has been demonstrated that gas can be manufactured by a large plant and distributed by means of a high-pressure service to smaller communities many miles distant, where it can be sold at a price much less than that at which it could be manufactured and distributed locally. This is a development which is certain to be of future importance but calls for more engineering skill than it has received.

Gas is becoming used more freely for industrial purposes, and this field should have the most careful consideration.

The man who is best equipped to improve and develop the gas business should have the knowledge of chemical and mechanical engineering that can be obtained at the Institute, and for such a man there should be a successful future in this industry.

SCIENTIFIC SOCIETIES.

REPORT OF THE SUB-COMMITTEE ON GLYCERINE ANALYSIS.¹

By A. C. LANGMUIR, Chairman, A. M. COMEY, ROBT. E. DIVINE, S. S. EMERY, J. W. LOVELAND, W. H. LOW.

As a result of some wide discrepancies in the analy-

¹ A sub-committee of The Committee on Fats, Soaps and Glycerine

sis of a crude glycerine sent out to a number of chemists, Mr. B. T. Babbitt Hyde suggested the application of standard methods of analysis to this field.

of the Division of Industrial Chemists and Chemical Engineers. The report has received the approval of the Supervisory Committee on Standard Methods of Analysis, American Chemical Society

Acting on this idea and extending its scope, Dr. W. F. Hillebrand, the chairman of the Committee on Uniformity in Technical Analysis, appointed early in 1908 a committee to investigate the methods used in testing fats, soap and glycerine, with a view to the development of standard methods of analysis.

The committee thus appointed, with W. D. Richardson as chairman, held its first meeting at New Haven on June 30, 1908. It was decided that the scope of the work be limited to the consideration of the analysis of such materials as are commonly bought and sold.

A number of sub-committees were appointed, among which was the Sub-Committee on Glycerine Analysis, consisting of the following gentlemen: A. C. Langmuir, Chairman, Robt. E. Divine and B. T. Babbitt Hyde. Mr. Hyde subsequently resigned in favor of Mr. Loveland. In 1909 three members were added to the committee, making its composition as follows:

A. C. Langmuir, Chairman, Supt. and Chemist, Marx & Rawolle, New York.

A. M. Comey, Director, Research Laboratory, Dupont Powder Co., Chester, Pa.

Robt. E. Divine, Glycerine Specialist, Detroit, Mich.

S. S. Emery, Chemist at the Louviers Plant of the Dupont Powder Co.

J. W. Loveland, Works Manager, B. T. Babbitt, Inc., New York.

W. H. Low, Chief Chemist, Cudahy Packing Co., So. Omaha, Neb.

In order that the glycerine trade might be informed of the work to be taken up and that we might learn the prevailing methods in use for the analysis of glycerine, a letter was drawn up and widely circulated among glycerine producers, refiners and chemists in the U. S., England and Europe. The letter was published in *THIS JOURNAL*, April, 1909, p. 268.

Two samples of crude glycerine and a prepared glycerine containing a known amount of anhydrous glycerine were then sent to a number of chemists for analysis, with a request that their method be returned with the report.

A meeting was held at Boston in Dec., 1909, to discuss the replies to the circular letter, the results of the analysis of the samples, and to outline the research work required. A full report of this meeting, together with a synopsis of the methods of glycerine analysis received, may be found in *THIS JOURNAL*, May, 1909, pp. 222-229.

A consideration of the methods turned in showed that the bichromate method was more commonly in use, but that there were apparently as many modifications as there were chemists using the process. The acetin method, although less frequently employed, was warmly recommended. It had suffered but little change from the original Benedikt and Cantor process.

The bichromate and acetin methods were the only ones referred to in our correspondence and we have not discovered that the acetone extraction, permanganate oxidation or determination as isopropylidide

are anywhere in general use in the analysis of crudes. Our committee has therefore confined its work to the examination of the two methods first named.

The bichromate method has in its various modifications traveled a long way from the original Hehner process and most of the changes made have diminished rather than improved the accuracy of the method. It will be shown that the effectiveness of different purifying agents in removing organic impurities varies greatly and yet there are in use: silver sulphate, copper sulphate, silver oxide, silver carbonate, silver acetate and basic lead acetate, either alone or in combination with some silver salt. The basic lead acetate is seldom prepared in the same way and is of varying basicity. To completely oxidize glycerine with bichromate in presence of the lower fatty acids, which escape the purification, without at the same time partially oxidizing the latter, is a problem requiring a nice adjustment of conditions. We find that widely varying proportions of sulphuric acid and bichromate are used and that the time of oxidation is not the same. These facts disclose an urgent need for standardization.

It is noteworthy that in all the work of the past on glycerine analysis, which has come to our notice, no checks have been made against pure anhydrous glycerine. In some cases dilute glycerine was used, but its strength was determined either by combustion, a method of little value, or by specific gravity and reference to one of the many specific gravity tables, most of which are inaccurate. The basis of all our researches on the bichromate and acetin methods has been a sample of anhydrous c. p. glycerine, which is shown to be practically anhydrous (within a few hundredths of a per cent.) by a large number of tests. By dilution of this glycerine a new specific gravity table has been prepared.

We have made a detailed series of experiments to establish the most favorable conditions to effect the complete oxidation of glycerine by bichromate. A comparative study has been made of the different purifying agents in use. The acetin method has also been examined at every stage and carefully compared with the bichromate on a number of crudes. Distillation tests have been made in a specially designed laboratory still giving quantitative results which have been compared with the chemical tests.

A paper giving the results of our earlier work was read by the chairman at the May meeting of the Chicago Section in 1910, but has not been published. The committee has held meetings at Lake Mohonk, June 18-20, at New York, Oct. 18, and at Chicago, Dec. 7-8, 1910. The last meeting was attended by Messrs. Allan and Tainsh, delegates from the British Committee on Glycerine Analysis. The British committee called an international conference on glycerine analysis at London, Oct. 25-27, 1910. Representatives from Germany and France were present. The American committee was represented by Mr. Emery and the chairman.

As a result of our researches we have unanimously decided that the acetin method is the basis on which

glycerine should be bought and sold. The bichromate method is of value in factory control and for routine work in the analysis of crudes of known good character. For this reason we have felt it necessary to retain the bichromate method, in a properly standardized form, but we advise against its use in general analytical work.

The British committee, with Dr. O. Hehner as chairman, arrived independently at the same conclusion as ourselves in regard to the respective merits of the two methods. The German committee was soon convinced of the greater accuracy of the acetin process. The international conference was therefore able to devote practically all of the time at its disposal to an exhaustive discussion of the details of the proposed methods. The method which is here given is an International method, inasmuch as the details have been agreed on by all the committees.

Neither the acetin nor the bichromate method is correct in theory or practice on crudes containing trimethylenglycol or polyglycerols. We only know that the acetin is less affected by these substances than the bichromate. They are not precipitated by basic lead acetate or silver salts and are therefore left to exert the full reducing power of the molecule on the bichromate. With the acetin on the other hand, action is proportional to the number of OH groups directly attached to the chain. For example, a crude glycerine containing 80 per cent. glycerol and 1 per cent. trimethylenglycol will show by the bichromate method 81.38% and by the acetin method 80.81 per cent. glycerol. With triglycerol, a 1 per cent. addition would increase the bichromate test by 1.15 per cent. and the acetin by 0.64 per cent. A comparison of the results obtained by the acetin and bichromate methods will therefore often throw light on the nature and quantity of the impurities present.

In the absence of a chemical method which will show glycerol only in such mixtures, we must therefore prefer the acetin method, because it gives the same results as the bichromate on pure glycerine and high-grade crudes and lower or much lower results on bad crudes. In the acetin method to be described the error caused by the presence of polyglycerols is partially offset by the determination of the acetylizable matter in the non-volatile residue at 160° C., which will hold the higher polyglycerols. The lower polyglycerols and trimethylenglycol are volatile at 160° C. and are therefore figured as glycerol. Trimethylenglycol is more volatile than glycerol and may be distilled off with the glycerine in the first portions of the distillate, where it may be determined by the spread between the acetin and bichromate tests.

We have met with some bad crudes which cannot with safety be analyzed by any chemical method known to us. The only method which will give even approximate results on crudes high in glycol or crudes containing still residues is a distillation in a still adapted to quantitative work. A crude containing

a large amount of glycol tested 81.8 per cent. (bichromate), 76.2 per cent. (acetin) and 71.0 per cent. (by distillation). A crude made from still residues showed 73 per cent. by the bichromate method, 48 per cent. by the acetin method, and only 30 per cent. by distillation. These are extreme cases, but serve to show that a marked spread between the acetin and the bichromate tests is an indication that both are probably incorrect.

The acetin test is not looked upon with favor by some chemists on the ground that results are unreliable unless precautions are taken out of the reach of the busy laboratory. This opinion is largely the result of erroneous statements in the text-books and literature. The danger of saponifying triacetin by standing in aqueous solution and during neutralization of the acetic acid is greatly exaggerated. A point in favor of the acetin method is the avoidance of the purification required by the bichromate test. Two of the members of this committee have made the change from the bichromate to the acetin test without any trouble, although they had but little experience with the latter. In their hands the acetin method has given results of greater uniformity and accuracy than the bichromate. Every member of our committee has had by this time some experience with the acetin in comparison with the bichromate method and a few of us have had a very extensive experience, covering several years. It is our opinion that with proper attention to details which are not in the least onerous, chemists will be able to obtain results which are more concordant than those obtainable by the bichromate method and at the same time nearer the actual glycerol present.

A standard method for glycerine analysis has been wanted for a long time, and in order to avoid delay we are publishing our methods in advance of the researches which have led to our conclusions. Papers will follow which will describe our experiments in connection with the acetin and bichromate methods, the quantitative distillation of glycerine, a specific gravity table for glycerine and specifications for c. p. and dynamite glycerine.

The chairman has a quantity of anhydrous c. p. glycerine, which he is prepared to distribute to chemists who wish to standardize their methods. This glycerine has been analyzed by most of the members of the British and American committees. A standard soap lye crude will also be prepared.

It is not possible to carry through as many acetin tests per day as bichromate, but with many crudes the difference between results is so wide, that it is not any longer a question as to which method is the quicker or more convenient. The great increase in the price of crude glycerine, together with a falling off in quality, due to the use of impure fats and greases as well as the introduction of new methods of saponification, make it impossible to defend the bichromate method on the ground of convenience and custom. Valuable as this method has been in the past, it is unable to cope with many crudes of to-day.

METHODS OF CRUDE GLYCERINE ANALYSIS.

Recommended by the International Committee.

SAMPLING.

The most satisfactory method available for sampling crude glycerine liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerine sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salt has taken place. In such cases he shall sample with a sectional sampler (see appendix) then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of the same made in his certificate, together with the temperature of the glycerine. Each drum must be sampled. Glycerine which has deposited salt or other solid matter cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerine to be taken including any deposit.

ANALYSIS.

1. *Determination of Free Caustic Alkali.*—Put 20 grams of the sample into a 100 cc. flask, dilute with approximately 50 cc. of freshly boiled distilled water, add an excess of neutral barium chloride solution, 1 cc. of phenolphthalein solution, make up to the mark and mix. Allow the precipitate to settle, draw off 50 cc. of the clear liquid and titrate with normal acid ($N/1$). Calculate the percentage of Na_2O existing as caustic alkali.

2. *Determination of Ash and Total Alkalinity.*—Weigh 2 to 5 grams of the sample in a platinum dish, burn off the glycerine over a luminous Argand burner or other source of heat,¹ giving a low temperature, to avoid volatilization and the formation of sulphides. When the mass is charred to the point that water will not be colored by soluble organic matter, lixiviate with hot distilled water, filter, wash and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate the water, and carefully ignite without fusion. Weigh the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator methyl orange cold or litmus boiling.

3. *Determination of Alkali Present as Carbonate.*—Take 10 grams of the sample, dilute with 50 cc. distilled water, add sufficient $N/1$ acid to neutralize the total alkali found at (2), boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube with distilled water, free from carbon dioxide, and then titrate back with $N/1$ NaOH, using phenolphthalein as indicator. Calculate the percentage of Na_2O . Deduct the Na_2O found in (1). The difference is the percentage of Na_2O existing as carbonate.

4. *Alkali Combined with Organic Acids.*—The sum of the percentages of Na_2O found at (1) and (3) de-

ducted from the percentage found at (2) is a measure of the Na_2O or other alkali combined with organic acids.

5. *Determination of Acidity.*—Take 10 grams of the sample, dilute with 50 cc. distilled water free from carbon dioxide, and titrate with $N/1$ NaOH and phenolphthalein. Express in terms of Na_2O required to neutralize 100 grams.

6. *Determination of Total Residue at 160° C.*—For this determination the crude glycerine should be slightly alkaline with Na_2CO_3 , not exceeding 0.2 per cent. Na_2O , in order to prevent loss of organic acids. To avoid the formation of polyglycerols this alkalinity must not be exceeded.

Ten grams of the sample are put into a 100 cc. flask, diluted with water and the calculated quantity of $N/1$ HCl or Na_2CO_3 added to give the required degree of alkalinity. The flask is filled to 100 cc., the contents mixed, and 10 cc. measured into a weighed Petrie or similar dish 2.5 in. in diameter and 0.5 in. deep, which should have a flat bottom. In the case of crude glycerines abnormally high in organic residue a smaller amount should be taken, so that the weight of the organic residue does not materially exceed 30 to 40 milligrams.

The dish is placed on a water bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven¹ measuring 12 ins. cube, having an iron plate 0.75 in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf half way up the oven. On these strips the dish containing the glycerine is placed.

If the temperature of the oven has been adjusted to 160° C. with the door closed, a temperature of 130° to 140° can be readily maintained with the door partially open, and the glycerine, or most of it, should be evaporated off at this temperature. When only a slight vapor is seen to come off, the dish is removed and allowed to cool.

An addition of 0.5 to 1.0 cc. of water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spurt. The time taken up to this point cannot be given definitely, nor is it important. Usually two or three hours are required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is

¹ An electric oven suitable for this work, which is readily adjusted to 160° C., has been made for Mr. Low and the chairman, by the Apparatus and Specialty Co., Lansing, Mich. Its size is 9½ × 10 × 16 inches and capacity 8 Petrie dishes. It gives a strong draft at constant temperature.

repeated until a constant loss of 1 to 1.5 mg. per hour is obtained.

In the case of acid glycerine a correction must be made for the alkali added, 1 cc. *N*/1 alkali represents an addition of 0.03 gram. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. The corrected weight multiplied by 100 gives the percentage of total residue at 160° C.

This residue is taken for the determination of the non-volatile acetylizable impurities (see acetin method).

7. *Organic Residue*.—Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. (it should be noted that alkaline salts of fatty acids are converted to carbonates on ignition and that the CO_2 thus derived is not included in the organic residue).

ACETIN PROCESS FOR THE DETERMINATION OF GLYCEROL.

This process is the one agreed upon at a conference of delegates from the British, French, German and American committees, and has been confirmed by each of the above committees as giving results nearer to the truth than the bichromate method on crudes in general. It is the process to be used (if applicable) whenever only one method is employed. On pure glycerines the results are identical with those obtained by the bichromate process. For the application of this method the crude glycerine should not contain over 60 per cent water.

REAGENTS REQUIRED.

(A) *Best Acetic Anhydride*.—This should be carefully selected. A good sample must not require more than 0.1 cc. normal NaOH for saponification of the impurities when a blank is run on 7.5 cc. Only a slight color should develop during digestion of the blank.

The anhydride may be tested for strength by the following method: Into a weighed stoppered vessel, containing 10 to 20 cc. of water, run about 2 cc. of the anhydride, replace the stopper and weigh. Let stand with occasional shaking, for several hours, to permit the hydrolysis of all the anhydride; then dilute to about 200 cc., add phenolphthalein and titrate with *N*/1 NaOH. This gives the total acidity due to free acetic acid and acid formed from the anhydride. It is worthy of note that in the presence of much free anhydride a compound is formed with phenolphthalein, soluble in alkali and acetic acid, but insoluble in neutral solutions. If a turbidity is noticed toward the end of the neutralization it is an indication that the anhydride is incompletely hydrolyzed and inasmuch as the indicator is withdrawn from the solution, results may be incorrect.

Into a stoppered weighing bottle containing a known weight of recently distilled aniline (from 10 to 20 cc.) measure about 2 cc. of the sample, stopper, mix, cool and weigh. Wash the contents into about 200 cc. of cold water, and titrate the acidity as before. This yields the acidity due to the original,

preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated to 100 grams) and double the result, obtaining the cc. *N*/1 NaOH per 100 grams of the sample. 1 cc. *N*/NaOH equals 0.0510 anhydride.

(B) *Pure Fused Sodium Acetate*.—The purchased salt is again completely fused in a platinum, silica or nickel dish, avoiding charring, powdered quickly and kept in a stoppered bottle or desiccator. It is most important that the sodium acetate be anhydrous.

(C) *A Solution of Caustic Soda for Neutralizing, of about N/1 Strength, Free from Carbonate*.—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

(D) *N/1 Caustic Soda Free from Carbonate*.—Prepared as above and carefully standardized. Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

(E) *N/1 Acid*.—Carefully standardized.

(F) *Phenolphthalein Solution*.—0.5 per cent. phenolphthalein in alcohol and neutralized.

THE METHOD.

In a narrow-mouthed flask (preferably round-bottomed), capacity about 120 cc., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1.25 to 1.5 grams of the glycerine. A Grethan or Lunge pipette will be found convenient. Add about 3 grams of the anhydrous sodium acetate, then 7.5 cc. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside diameter. The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used it should have had a preliminary treatment with hot acetic anhydride vapor.

Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat, and through the condenser tube add 50 cc. of distilled water free from carbon dioxide at a temperature of about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapors from the flask on adding water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment, bearing in mind that the anhydride in excess is much more effectively hydrolyzed in hot than in cold water. The contents of the flask may be warmed to, but must not exceed, 80° C., until the solution is complete, except a few dark flocks repre-

senting organic impurities in the crude. By giving the flask a rotary motion, solution is more quickly effected.

Cool the flask and contents without loosening from the condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off the stopper or ground glass connection into the flask, and filter the contents through an acid-washed filter into a Jena glass flask of about 1 liter capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 cc. of phenolphthalein solution (F), then run in caustic soda solution (C) or (D) until a faint pinkish yellow color appears throughout the solution. This neutralization must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralized, as indicated by the slower disappearance of the color developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 cc. or a calculated excess of $N/1$ NaOH (D) and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate the excess of NaOH with $N/1$ acid (E) until the pinkish yellow or chosen end-point color just remains.² A further addition of the indicator at this point will cause an increase of the pink color; this must be neglected, and the first end-point taken.

From the $N/1$ NaOH consumed calculate the percentage of glycerol (including acetylatable impurities) after making the correction for the blank test described below.

1 cc. $N/1$ NaOH = 0.03069 gram glycerol.

The coefficient of expansion for normal solutions is 0.00033 per cc. for each degree centigrade. A correction should be made on this account if necessary.

Blank Test.—As the acetic anhydride and sodium acetate may contain impurities which affect the result, it is necessary to make a blank test, using the same quantities of acetic anhydride, sodium acetate and water as in the analysis. It is not necessary to filter the solution of the melt in this case, but sufficient time must be allowed for the hydrolysis of the anhydride before proceeding with the neutralization. After neutralization it is not necessary to add more than 10 cc. of the $N/1$ alkali (D), as this represents the excess usually present after the saponification of the average soap lye crude. In determining the acid equivalent of the $N/1$ NaOH, however, the entire amount taken in the analysis, 50 cc., should be titrated after dilution with 300 cc. water free from carbon dioxide and without boiling.

² A precipitate at this point is an indication of the presence of iron or alumina, and high results will be obtained unless a correction is made as described below.

Determination of the Glycerol Value of the Acetylatable Impurities.—The total residue at 160° C. is dissolved in 1 or 2 cc. of water, washed into the acetylizing flask and evaporated to dryness. Then add anhydrous sodium acetate and acetic anhydride in the usual amounts and proceed as described in the regular analysis. After correcting for the blank, calculate the result to glycerol.

INSTRUCTIONS FOR CALCULATING THE ACTUAL GLYCEROL CONTENT.

(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylatable impurities if any are present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylatable impurities are present these are included in this figure.

Trimethylenglycol is more volatile than glycerine and can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and bichromate results on such distillates. The spread multiplied by 1.736 will give the glycol.

BICHROMATE PROCESS FOR GLYCEROL DETERMINATION.

REAGENTS REQUIRED.

(A) *Pure potassium bichromate* powdered and dried in air free from dust or organic vapors, at 110° to 120° C. This is taken as the standard.

(B) *Dilute Bichromate Solution.*—7.4564 grams of the above bichromate are dissolved in distilled water and the solution made up to one liter at 15.5° C.

(C) *Ferrous Ammonium Sulphate.*—It is never safe to assume this salt to be constant in composition and it must be standardized against the bichromate as follows: dissolve 3.7282 grams of bichromate (A) in 50 cc. of water. Add 50 cc. of 50 per cent. sulphuric acid (by volume), and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (B). Calculate the value of the ferrous salt in terms of bichromate.

(D) *Silver Carbonate.*—This is prepared as required for each test from 140 cc. of 0.5 per cent. silver sulphate solution by precipitation with about 4.9 cc. $N/1$ sodium carbonate solution (a little less than the calculated quantity of $N/1$ sodium carbonate should be used as an excess prevents rapid settling). Settle, decant and wash once by decantation.

(E) *Subacetate of Lead.*—Boil a 10 per cent. solution of pure lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(F) *Potassium Ferricyanide.*—A very dilute, freshly prepared solution containing about 0.1 per cent.

THE METHOD

NOTES.

Weigh 20 grams of the glycerine, dilute to 100 cc. and take 25 cc. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and add a slight excess (about 5 cc. in most cases) of the basic lead acetate (E), allow to stand a few minutes, dilute with distilled water to 100 cc., and then add 0.15 cc. to compensate for the volume of the precipitate, mix thoroughly, filter through an air-dry filter into a suitable narrow-mouthed vessel, rejecting the first 10 cc., and return the filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate (in the great majority of cases 5 cc. are ample, but occasionally a crude will be found requiring more, and in this case another aliquot of 25 cc. of the dilute glycerine should be taken and purified with 6 cc. of the basic acetate). Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 cc. of the clear filtrate into a flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3.7282 grams of the powdered potassium bichromate (A). Rinse down the bichromate with 25 cc. of water and let stand with occasional shaking until all the bichromate is dissolved (no reduction will take place in the cold).

Now add 50 cc. of 50 per cent. sulphuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapors, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (C), making spot tests on a porcelain plate with the potassium ferricyanide (F). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 gram glycerol = 7.4564 grams bichromate.

1 gram bichromate = 0.13411 gram glycerol.

The percentage of glycerol obtained above includes any oxidizable impurities present after the purification. A correction for the non-volatile impurities may be made by running a bichromate test on the residue at 160° C.

(1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulphuric acid, as stipulated.

(3) For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth and the basic lead acetate to 0.5 cc.

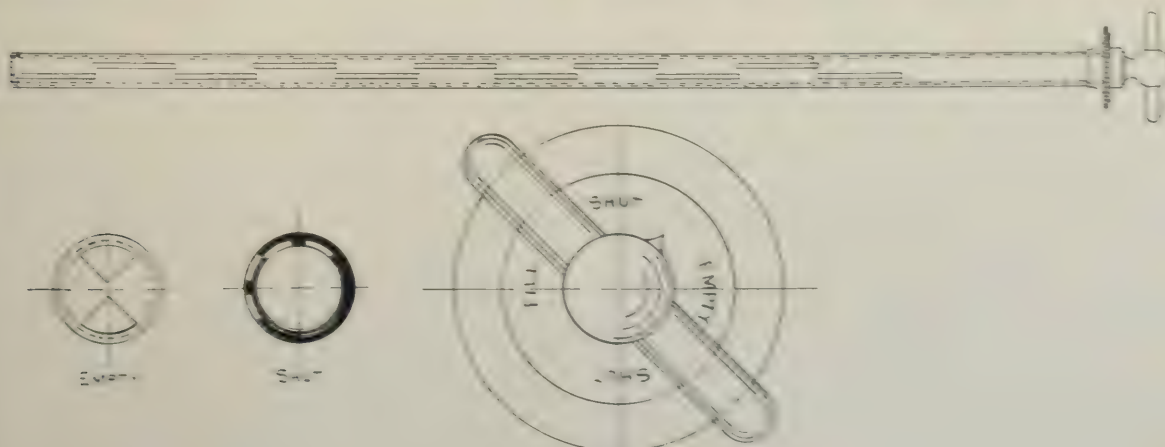
(4) It is sometimes advisable to add a little potassium sulphate to insure a clear filtrate.

APPENDIX.

SAMPLING CRUDE GLYCERINE.

The usual method of sampling crude glycerine hitherto has been by means of a glass tube, which is slowly lowered into the drum with the object of taking as nearly as possible a vertical section of the glycerine contained in the drum. This method has been found unsatisfactory, owing to the fact that in cold climates glycerine runs into the tube very slowly, so that, owing to the time occupied, it is impossible to take a complete section of the crude. Another objection to the glass tube is that it fails to take anything approaching a correct proportion of any settled salt contained in the drum.

The sampler which is illustrated herewith has been devised with the object of overcoming the objections to the glass tube as far as possible. It consists of two brass tubes, one fitting closely inside the other. A number of ports are cut out in each tube in such a way that when the ports are opened a continuous slot is formed which enables a complete section to be taken throughout the entire length of the drum. By this arrangement the glycerine fills into the sampler almost instantaneously. There are a number of ports cut at the bottom of the sampler which render it possible to take a proportion of the salt at the bottom of the drum. The instrument is so constructed that all the ports, including the bottom ones, can be closed simultaneously by the simple action of turning the handle at the top; a pointer is arranged which indicates on a dial when the sampler is open or closed. In samplers of larger section (1 in.) it is possible to arrange a third motion whereby the bottom ports



only are open for emptying, but in samplers of smaller dimensions ($\frac{5}{8}$ in.) this third motion must be dispensed with, otherwise the dimensions of the ports have to be so small that the sampler would not be efficient.

In using the sampler it is introduced into the drum with the ports closed, and when it has touched the bottom, the ports are opened for a second or two, then closed and withdrawn, and the sample discharged into the receiving vessel by opening the ports. When the drum contains salt which has deposited, the ports must be opened before the sampler is pushed through the salt, thus enabling a portion to be included in the sample. It is, however, almost impossible to obtain a correct proportion of salt after it has settled in the drum and it is therefore recommended that the drum be sampled before any salt has deposited. A sampler 1 in. in diameter withdraws approximately 10 oz. from a 110-gal. drum. A sampler $\frac{5}{8}$ in. in diameter will withdraw about 5 oz.

PRELIMINARY REPORT OF THE COMMITTEE ON QUALITY OF PLATINUM LABORATORY UTENSILS.¹

In compliance with the authorization accompanying the formation of the above-named committee at the Minneapolis meeting its membership was completed by the selection of Dr. E. T. Allen, of the Geophysical Laboratory, Carnegie Institution.

The committee immediately began to seek information by sending copies of the subjoined letter to the following American firms, who were known or supposed to be or to have been engaged in the manufacture of platinum ware: J. Bishop & Co. Platinum Works, and John C. Entriken, Malvern, Pa., Baker & Co., Inc., American Platinum Works, and Croselmire and Ackor Co., Newark, N. J.

WASHINGTON, D. C.,

January 27, 1911.

Gentlemen:

The Division of Industrial Chemists and Chemical Engineers of the American Chemical Society, when in session at Minneapolis on the last days of December, 1910, established a committee to study the question of the quality of platinum ware and to report, if possible, at the Indianapolis meeting in the summer of 1911, specifications for the benefit of the consumer. The members of this committee are:

Wm. F. Hillebrand, Bureau of Standards; Percy H. Walker, Bureau of Chemistry; and Eugene T. Allen, Geophysical Laboratory, Carnegie Institution, Washington, D. C.

It is well known to most chemists that the quality of much, if not all, of the chemical platinum ware made in this country in recent years is markedly inferior to that which was procurable many years ago. It is probable that the inferiority has not arisen suddenly. In part, it may have existed formerly and has been discovered only recently; in part it has come about slowly, so that chemists of the younger genera-

tion have had less opportunity for comparison than those who have been active for many years. Hence the protest against the quality of much of the present day ware has been slow to crystallize.

The objections made to inferior ware, so far as registered up to now, may be stated as follows:

- (1) Undue loss of weight on ignition.
- (2) Undue loss of weight on acid treatment, especially after strong ignition.
- (3) An unsightly appearance of the surface of the ware after strong ignition, especially in the early stages of heating.
- (4) Adherence of crucibles and dishes to triangles sometimes to such an extent as to leave an indentation of the vessel at the points of contact with the triangle, even when complete cooling has been reached before the two are separated from one another.
- (5) Alkalinity of the surface of the ware after strong ignition.
- (6) Blistering.
- (7) Development of cracks after continued heating.

As causes for (1), an undue loss on ignition, have been pretty generally suggested a content of iridium and perhaps of base metals of low boiling point.

Causes for (2), loss on acid treatment after ignition are known to reside in an iron content in the first place, and in a content of an alkaline-earth metal (calcium) in the second, these being brought slowly to the surface and there oxidized, so as to give in extreme cases a reddish coating of ferric oxide on the one hand and an alkaline reaction on the other.

The cause of the unsightly surface aspect of the ware in the early stages of treatment (3) is sometime due to volatile impurities but later seems to be caused by crystallization of the platinum. The question arises: to what extent is this crystallization caused by the presence of an impurity, for instance of a metal giving an alkaline oxide, and consequently, to what extent can it be reduced, if at all, by complete elimination of the impurity?

As to (4), adherence of vessel to triangles, to what extent is this due to an inferior quality of the triangle as contrasted with the vessel, and would it be apparent if the quality of both were good and equally good?

As to (5), alkalinity after ignition, it may be said that its cause is, of course, a factor in the loss on acid treatment after ignition.

Blistering (6) is a defect of long standing and of somewhat infrequent occurrence, and development of cracks (7) is of far too common occurrence.

It will be evident that the investigation of the subject entrusted to the committee involves a wide field and in order that its report may have the largest measure of value, *i. e.*, be constructive instead of merely critical, it is very important that the willing coöperation of manufacturers of platinum ware intended for chemical use shall be secured with a view to remedying the above indicated defects, and others if they exist.

The first purpose of this letter is to ascertain if your

¹ Presented at the Indianapolis Meeting before the Division of Industrial Chemists and Chemical Engineers.

firm is willing to aid the committee by furnishing such information as it may need in regard to the sources of the platinum entering into different kinds of ware, the methods of refining and the mechanical and chemical treatment to which the platinum is subjected at each step of the processes of conversion into finished ware. The committee would be willing to regard such information as strictly confidential if so requested. With it, progress toward valid conclusions and suggestions would be speedy; but without it, slow and uncertain for lack of adequate and precise data. It is hoped therefore that each American manufacturer of chemical platinum ware will send a thoroughly competent technical delegate to confer with the committee, either in Washington or at some central place to be decided on by mutual agreement.

By such conference at first hand with the firm's representatives, singly or collectively, as may be preferred, it is hoped that simple specifications can be drawn for the consumers' use which it will be quite possible for the manufacturers to meet. This is a case where it is manifestly impossible for the consumer to require from the manufacturer a material of prescribed composition, for he has not at his command the necessary data to serve as a basis for specification, whereas these data are, or should be, at least partly, in possession of the manufacturer. The committee feels strongly that the consumer needs immediate help, and also that the manufacturer can do no greater service to himself than by full and free co-operation with the committee on behalf of the consumer. The alternative will be, no doubt, a large increase in the existing demand for foreign wares in preference to that of American manufacture.

Kindly indicate in some detail your willingness or unwillingness to meet with the committee and to forward its aims as above set forth.

The above inquiries brought forth the information in the first place that John C. Enriken no longer manufactured platinum ware and that Croselmir & Ackor Co. have no manufacturing plant in America. The remaining firms met the request of the committee for interviews by sending separately representatives to Washington. From the lengthy conferences held, considerable information was obtained regarding the sources of the ore and ingot metal that are worked up in this country, their degree of purity, and the processes of refining and manufacture to which they are subjected. Interesting as much of this information was, the committee does not deem it necessary for the purpose of this report to reproduce in detail even that which was not confidential in character. To judge from the claims made, the composition of ordinary American-made crucibles and dishes differs widely with different manufacturers, ranging with respect to iridium from 0.5 per cent. or less to 3 per cent. One maker admitted an iron content of 0.2-0.3 per cent. Little definitely was learned as to the percentages of other impurities. There was manifest a reticence in reply to certain questions, but the committee has a strong impression, supported by other evidence than that brought out in the conferences,

that in the past practically no far-reaching refining of ore or imported metal has been practiced in this country, and that, in spite of some statements to the effect that scrap was not worked over for chemical ware, this has been done both at home and abroad, that the practice continued through years has contributed in no small degree to the acknowledged inferiority of most modern chemical ware used in this country, and that this inferiority will increase in degree with time unless stopped. It was admitted by one at least that the sharp competition of recent years was responsible in part for lack of proper control of the composition of chemical ware.

Since it was not possible for the committee to begin its study by making careful analyses of a variety of samples of ware on the market, the most promising line of attack seemed to be to secure samples of their ordinary commercial ware from all the domestic manufacturers, and also if possible of metal specially refined by themselves. These it was proposed to compare among themselves and with foreign-made ware as to behavior on heating, both as regards appearance and stiffness, loss in weight, and tests for iron and alkali. As standards for comparison were taken one crucible from Heraeus, of his own make, of "Thermoelement" platinum, which is claimed to be free from all impurities, and three of his "Tiegel" platinum, containing according to the latest information not over 0.05 per cent. iridium and probably less. These last were made up by one of the American firms, but had a shape different from the crucible of "Thermoelement" platinum made by Heraeus, which it may be remarked belonged to the Bureau of Chemistry.

All the makers expressed themselves as ready to furnish for test several crucibles and triangles of their ware, ordinary and specially refined. Not all of these have been received up to the present time, and if there were no other ground the committee is on this account unable to offer now a complete report.

In order to study the effect of ordinary laboratory conditions, the first tests were made over blast-lamps. It was soon found that the temperatures obtained were markedly dependent on the construction of the lamps and on the gas pressure. Hence, for later tests over blast-lamps one of high efficiency was chosen, giving a temperature, measured by thermocouple, of 1200-1210° in the lower part of the crucible when the crucible was covered, and of about 1100° in the upper part just under the perforated lid, and this lamp alone was afterwards used. The variations of gas pressure could not be overcome conveniently. For this reason, and also to test the continued mechanical and chemical effect of the blast flame in causing loss in weight, it seemed necessary to try the effect of electrical heating. The construction of a resistance furnace that will meet the exacting requirements of the tests contemplated has been found more difficult than was anticipated and is not yet wholly achieved. This is another reason why the committee's report is only preliminary and partial.

The committee is aware that considerable testing of platinum ware has been done by a number of writers¹ and that a portion of the field covered by it has been gone over already by them. As a rule, however, no comparison was made between the ware of different makers, and temperatures were not always controlled by measurement. Further, the experiments were restricted, in the main, to determining losses on ignition. The committee will make no further reference in this report to the work of others, reserving this for a later occasion.

EXPERIMENTAL DATA.

DISCUSSIONS.

Surface Aspect of Ware after Heating.—Leaving out of account the discoloration due to the oxidation of iron, the surface indications shown by ware that has come under the observations of the committee at different times are not easy to describe.

With good ware the crucible becomes uniformly affected by the blast when this envelopes the whole vessel, either taking on a whitish, frosted appearance or becoming uniformly mottled inside and out with crystal plates which do not all reflect the light alike. There is great difference in the size of these plates, from almost microscopic in the case of the frost-like aspect noted to those that are easily apparent to the naked eye. Sometimes, when the plates are large, a decided blue color is imparted to the surface. The crucible of "Thermoelement" platinum of Heraeus which was tested showed only the frosted surface, while his "Tiegel" platinum became in every case coarsely marked. No explanation for this difference has yet been offered, a difference that seems surprising in view of the supposed very slight differences in composition of the two.

On poor ware the surface becomes more or less whitish, sometimes faintly brownish in places, but the discolorations are not uniformly distributed and they often impart an unsightly appearance. As a rule, the lower part of the crucible, where it was hottest, remains bright and from it stretch out more or less fan-shaped areas, the direction of which is affected by that of the flame, *i. e.*, whether this was inclined or applied vertically. The areas often have the appearance of sublimates, such as are produced on charcoal before the blowpipe. Now and then they have been seen starting sharply from a point. On direct and continued application of the flame their appearance and location may undergo change, and they may even disappear entirely.

Surface Alkalinity.—Concerning this singular phenomenon, which was first observed by Dr. H. C. P. Weber, of the Bureau of Standards, before the committee was organized, little definite information has thus far been gained. When manifest it can be de-

tected by applying moist red litmus paper to the surface of the vessel after it has been blasted for several hours. It has been noted in varying degrees of intensity and is not always apparent. The element producing the alkalinity is calcium. Its source might be lime from the crucibles used for melting the platinum or a lime salt used in polishing. Opinions as to this were conflicting, and the committee has not yet enough evidence at hand to warrant an expression of opinion of its own. The question is to be tested in part by comparison of ware that has been polished with Vienna lime and that which has not been so treated. What effect, if any, the presence of lime has on the quality of the ware is not known although the observations of Mylius and Hüttner and of Hillebrand² have direct bearing on this point.

Iron Content.—Rouge is sometimes used for polishing ware, and steel enters into its manufacture at more than one stage. These may account for a portion of the iron content of all ordinary ware and for the minute traces that may occur in the specially refined ware, but the evidence all goes to show that the introduction from this source (unless possibly when hot rolling of sheet and hot shaping of utensils is practiced) accounts for but a small fraction of the amount actually present. Its probable sources have already been indicated.

The committee has found that the "Thermoelement" and "Tiegel" platinum of Heraeus are satisfactory with respect to iron. It is either not detectable after long blasting or gives such a faint reaction as to represent a negligible quantity. One American firm has submitted what is claimed to be its own refined ware, which seems to be with respect to iron the equal of the "Tiegel" platinum of Heraeus.

So far as the experience of the members of the committee goes, all the ware supplied by American manufacturers as of their own make, during recent years has been strongly contaminated by iron. Sometimes its amount has been so great as to reveal itself after less than a half hour's exposure to a Bunsen burner flame, by a darkening, even reddening, of the inside of the crucible. More often the color change becomes pronounced only after long blasting. In an extreme case as much as 6 milligrams of iron oxide were removed from the surface of a 22-gram dish of German make some years ago by one of the committee members. An amount less than one milligram in weight suffices to impart a very dark color to a crucible of 20 cubic centimeters capacity. Even when the iron does not reveal itself thus, treatment with pure hydrochloric acid or with alkali pyrosulphate will often do so. Renewed heating will invariably bring more iron to the surface of the platinum if originally present. If the heating is done electrically instead of over a blast flame the color change due to iron oxide appears outside as well as inside the crucible. In one case, a few years ago, a dark color due to iron oxide was observed on ware as received from the maker.

Loss in Weight on Ignition.—Aside from a conten-

¹ Of experimenters in recent years the following may be mentioned: R. W. Hall, *J. Am. Chem. Soc.*, **22**, 494 (1900); Holborn and Henning, *Sitzb. Preuss. Akad. Wiss.*, **1902**, p. 936; Holborn and Austin, *Ibid.*, **1903**, p. 245; Hulett and Berger, *J. Am. Chem. Soc.*, **26**, 1512 (1904); W. C. Heraeus, *Ztschr. angew. Chem.*, **1907**, p. 1892; Mylius and Hüttner, in the general reports of the Phys. Tech. Reichsanstalt, *Ztschr. f. Instrumentenkunde*, **1906-1910**. Hall's paper seems to have been overlooked by the later writers.

² *Ztschr. Instrumentenkunde*, **30**, 190 (1910).

² *Bull.* **422**, U. S. Geol. Survey, p. 122.

of volatile base metals, iridium is supposed to be the volatile constituent of platinum which contributes chiefly to the observed loss of weight on strong ignition. This belief is supported by the experience of the committee.

The following set of tests on the ordinary commercial ware submitted by one firm is perhaps typical in general for a grade of ware that is supposed (from the statements made to the committee) to carry about 0.5 per cent. iridium, but further confirmative tests must be made before final conclusions are reached.

A crucible, weighing without cover about 16 grams, lost in four hours, over a vertical blast, 3.4 mg. The temperature inside the crucible and near the bottom was 1180°–1190° C. The rate of loss per hour was 0.85 mg. At 1100° the loss in less than four hours was 1.2 mg., or at the rate of somewhat over 0.3 mg. per hour.

Another crucible of the same lot, but slightly heavier, suffered a loss over the blast in 3 hours at 1200°–1210° of 2.3 mg. (0.77 mg. per hour) and of 1.9 mg. in addition at 1110° in 4.5 hours (0.42 mg. per hour). The surface of the crucible was very unevenly and strongly frosted, in marked contrast to the crucible of refined metal.

Other tests by one of the committee, on purchased domestic ware, showed losses of the same order, in some cases fully 1 milligram per hour at or near 1200°.

Contrasted with these, the "Tiegel" platinum of Heraeus above referred to shows to decided advantage. A crucible weighing about 16 grams lost in 12 hours (heatings of 4 hours each) 2.3 mgs. (0.2 mg. per hour) at temperatures not exactly known but approximating 1200°. At 1100° the loss was 0.9 mg. in 8 hours (0.11 mg. per hour). Another lost at the same rate as the first in 8 hours at 1190°–1210°.

Marked improvement was shown also by crucibles made of metal specially refined in this country, free from iron, and submitted by one firm, the rate of loss per hour being 0.3 mg. at 1200° in 12 hours, and 0.1 mg. at 1100° in 8 hours. The losses in the several periods of heating at 1200° were irregular, due perhaps to marked variations in atmospheric conditions, causing errors in weighing.

The crucible of "Thermoelement" platinum lost in 14 hours at 1200° 2.3 mg. (0.17 mg. per hour), and in 4 hours, at 1100°, 0.2 mg. (0.05 mg. per hour).

The triangles furnished with the crucibles, and of the same composition, suffered corresponding losses.

The last test shows that at the temperatures employed and over a blast-lamp even platinum that is claimed to be free from iridium has a perceptible vapor pressure or forms a volatile oxide, and it is also apparent that for chemical use the "Tiegel" platinum seems to be quite as satisfactory in quality.

The foregoing data may be summarized as follows:

	Rate of loss per hour at	
	1200°	1100°
Ordinary ware	0.85	0.3
"Tiegel" platinum	0.2	0.11
"Thermoelement" platinum	0.17	0.05
American refined ware	0.3	0.1

These data are not to be taken as rigidly exact, but they are probably fairly indicative. It should be remembered that the crucibles were not polished or wiped between the separate heatings.

From the above and other tests it may be inferred also that there is a sharp rise in the volatility curve for iridium and apparently for platinum also between the temperatures 1100° and 1200°. This point it is the intention of the committee to investigate further. If true, it would seem that for temperatures up to 1100° the volatility loss is of little significance with refined ware, but that it may be of some moment with ordinary commercial ware low in iridium and free from volatile base metals. At higher temperatures and with long-continued heating, however, the losses are appreciable even with the purest ware and are very high with commercial ware.

In this connection it is proper to say that in all probability the maximum temperature of the blast used in the above experiments is above that commonly attained in most laboratories. The gas used was artificial. Attention may be called also to the fact that relatively few substances obtained in chemical analysis require blast ignition and that blasting of an hour's duration is seldom necessary, so that in the majority of cases the volatility loss may be ignored.

Relative Stiffness and Hardness of Ware.—Pure platinum is soft and lacks stiffness. For these reasons it has been common practice to leave a certain amount of iridium in ware made from it or even to add to the amount already present. This addition is especially pronounced in triangles, which may contain 15–20 per cent. of iridium. The crucibles of "Tiegel" platinum made up in this country and also those of American-refined metal showed lack of stiffness in a very objectionable degree. In contrast with them was the crucible of "Thermoelement" platinum which, though not so stiff as the crucibles of commercial ware, was sufficiently so for all practical purposes. The reason for this difference is not yet apparent, but it may be due to the different shape of the crucibles or to a different thickness of the metal. If so the defect mentioned in the American crucibles tested is one that can be easily remedied by the makers.

Triangles.—In order that no error might be introduced by the use of triangles differing in composition from the crucibles, whereby iridium or other metal might pass from the former to the latter, the makers were asked to furnish with the crucibles triangles of the same composition, and this they did.

The refined crucibles and triangles were found to stick together badly while hot, owing to the welding property of pure platinum. They could be separated when cool, but often only by the expenditure of some

force and with danger of tearing out metal from the crucibles. It is probable that, in order to help maintain as far as possible the purity of a vessel of highly refined platinum, it should not be used in conjunction with a platinum triangle of different quality. Sagging, to a much greater degree than with ordinary triangles that have been some time in use, was not observed. The sticking defect is serious enough to take into consideration with refined ware. Therefore, experiments were made to test the temperatures obtainable inside a crucible with triangles of different materials and shapes. Without entering into details, it may be said that with a vertical blast flame the differences were far less than had been expected between triangles of platinum, of clay and of quartz, so that except for particular uses platinum triangles seem to have little advantage over those of clay or quartz when used under the conditions of the tests. The clay triangles with projecting points on which the crucibles rest allow as high a temperature to be reached in the upper part of the crucible as those of platinum. Quartz triangles made in one piece are to be had, but the cheaper ones of nickel or "nichrome" covered with quartz tubing are probably just as serviceable.

A word of caution may be added here with regard to the use of "nichrome" in direct contact with platinum. It has not been shown that there is no contamination from this source and in view of the cost of platinum ware any additional source of contamination is to be guarded against.

Blistering.—The blistering of crucibles seems to be far less frequent now than it was some years ago. It is probable that this defect resulted from past methods of manufacture rather than from other causes, and the committee has not given experimental attention to the subject.

Cracking.—One manufacturer attributed cracking not to the faulty nature of the ware but to careless handling of magnesium-ammonium phosphate, etc., and to heating with reducing flames. Another treated the ware mechanically to lessen the tendency to crack.

Extra Cost of Refined Ware.—The refining of platinum to the extent shown by the "Tiegel" platinum of Heraeus and by the recent product of one of the American manufacturers necessitates a higher charge than we have been accustomed to pay for commercial ware. In the experience of those who have bought the refined ware in this country the extra cost is in the neighborhood of 30 cents per gram. This is a large relative increase, but not excessive in comparison with the advantage gained from having an article that one knows to be free from all objectionable impurities in significant amounts. If platinum can be refined to the extent of removing all or nearly all iron and other base metals without removing all the iridium, the presence of the latter might be no disadvantage when extreme temperatures are not called for. The matter is important, for stiffness is essential to large vessels, and this quality iridium undoubtedly

imparts to platinum ware. That iron can be removed without removing the iridium the following experience of one of the committee at the Bureau of Standards appears to show. For the sake of completeness data not relevant to the point in question are included.

Two crucibles, No. 65, bought in 1905, and No. 117, bought from another firm in 1908, but never before, were first heated electrically at 1250° for several hours. No. 65 showed then no iron, or at most a trace, and lost weight subsequently over a blast at 1100°–1200° at the rate of 0.64 mg. per hour. Crucible No. 117 yielded 1.4 mg. iron after the electrical heating. After cleaning, subsequent blast ignition caused a loss at the rate of 0.7 mg. per hour for the first 3 hours and of 0.9 mg. for the next 8 hours; the surface became strongly alkaline and showed more iron oxide. From the stiffness of the crucibles and their high loss in weight it is practically certain that both contained iridium, yet one was free from iron, the other heavily charged. The original source of crucible No. 65 is not known.

CONCLUSIONS AND RECOMMENDATIONS.

Although it were premature to offer anything in the way of recommendations, the investigation has brought out certain facts and observations which the committee has deemed it wise to lay before chemists in the foregoing pages without waiting for completion of the inquiry. It is hoped that further study on domestic and foreign ware and a closer study of the literature will enable it to present a more finished report later.

It has been shown that ware of foreign make can be had against which nothing can be brought on the score of iron or other base metal content and in view of the loss caused by strong blasting seems to be safe of platinum itself and to be entirely negligible, for ordinary purposes, up to at least 1100°.

It appears also that American-refined platinum ware can be had of nearly if not quite as good quality and there does not seem to be any reason to think that its quality cannot be still further improved. There is a call for it to be done.

In order to obtain such ware it is only necessary to specify that it must show no marked uneven discoloration on heating and must give no test for iron after prolonged ignition (two hours may be regarded as sufficient) and that the rate of loss per hour at 1100° C. over a period of not less than four hours and considerably longer, shall not exceed, say 0.2 milligram. The makers are granted a fair margin of safety in the latter item. Ware which does not meet these conditions should not be accepted if the purchaser is willing to pay the enhanced cost of the better ware. These specifications are subject to revision.

In conclusion, for the present, the committee enters its thanks to the manufacturers who were interviewed, and especially to those who submitted samples for test. All of them expressed a desire to further

the objects of the committee's investigation and to furnish ware of the best quality, which each asserted his ability to do.

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THE DETERMINATION OF NITROGEN IN COMMERCIAL AMMONIATES OF HIGH NITROGEN CONTENT.

First Report of the Committee on Nitrogen Determination of Fertilizer Chemists, American Chemical Society.

In the fall of 1909, the attention of this committee was directed to the frequent discrepancies between the results of analyses by buyers' and sellers' chemists on samples representing shipments of high-grade commercial ammoniates, especially dried blood. The difference was remarkable in its tendency to higher results by the buyer's chemist. A typical example of this condition was shown in the joint analysis of a sample of dried blood prepared by a seller's chemist, as shown in the following table:

Analyst	Moisture	Ammonia	Nitrogen moisture free	
			Nitrogen	free
1	8.12	17.55	14.48	15.28
2	8.92	17.52	14.48	18.29
3.....		17.48	14.40	
4	8.12	17.90	14.74	15.84
5	4.74	17.87	14.72	15.45
6	4.95	17.85	14.70	15.47

Analysts 1, 2 and 3 are sellers' chemists, 4, 5 and 6 represent buyers'.

This table shows several important features. It must be borne in mind that payment is not and cannot be justly based on the analysis on a moisture-free basis. While therefore the latter may be considered the best basis of comparison from an analytical standpoint, so long as only the ammonia or nitrogen content is being compared, the actual ammonia or nitrogen content of the sample is the only real point of contention from a commercial standpoint. From the table it will be seen that the buyers' chemists find, on an average, 0.35 per cent. of ammonia or 0.29 per cent. of nitrogen more than the sellers' chemists. Assuming that the value of dried blood is \$3.00 per "unit" (per cent. of ammonia per ton), there is a difference of \$1.05 in the value per ton based on the respective average analyses obtained. From an analytical standpoint, after reducing the results obtained to a moisture-free basis, this difference is reduced somewhat, namely to 0.23 per cent. ammonia or 0.19 per cent. of nitrogen, but this fact does not alter the commercial discrepancy in the least.

The question at once arose: Is this difference due to differences in men or methods? The samples, particularly in the example quoted, were presumably prepared with every care to make them uniform. To answer the question, if possible, this committee decided to prepare samples of several ammoniates in sufficient quantity, and to obtain the true moisture and nitrogen content of these samples, so that they might serve the important purpose of standard samples. It is only by means of such standard samples that any chemist is able to judge the accuracy of his own work or that of his assistants, and it is not fair

to condemn any method unless such standards are available for final judgment, after the necessary experience with the method in question has been acquired.

Two samples were therefore prepared: one of dried blood, the other of high-grade tankage. To these a third was added later, representing a complete fertilizer composed of the dried blood mentioned above, acid phosphate and muriate of potash. After grinding the samples to a suitable degree of fineness, they were divided as follows: The entire sample was thoroughly mixed in a mechanical mixer, and divided into a number of containers while the mixer was running, placing a spoonful at a time into each container in turn. When the entire sample was divided in this way, the same number of fresh containers was set up and the contents of each container of the first set, after thoroughly mixing, was distributed into the second set as before. Finally each container of the second set was emptied on a porcelain tile, the contents thoroughly mixed, and divided into as many approximately equal parts as there were bottles to fill. Each part was then transferred to one of the bottles.

Requests for coöperative work were sent to all those who had registered in the Division of Fertilizer Chemists and to a number of other chemists, in order to obtain results by all the different methods possible, including the absolute or cupric oxid method and the soda-lime method as well as the various "wet combustion" methods.

To those who signified their willingness to coöperate, a set of the samples was sent together with the following instructions:

"It has been brought to the attention of this committee that there are frequently considerable differences between the analyses by various laboratories on the same shipments of high-grade nitrogenous materials, such as blood, tankage, etc. In order to throw light on this matter, it has been decided to send out to those who are willing to coöperate, three samples which have been prepared very carefully so as to ensure uniformity, and a set of these is being mailed to you under separate cover.

"These samples have been passed through a forty-mesh sieve and the determination should be made on them as received without further reduction or grinding. When weighing, the entire contents of each bottle should be spread on a sheet of glazed paper, and after mixing well, the portions for analysis should be taken from the sample thus spread out, while it is well mixed, so as to obtain truly representative analyses. There is more or less tendency to segregation in samples of this kind, and this is particularly true of the mixed fertilizer.

"In each of these three samples moisture and nitrogen are to be determined by the method or methods commonly in use in your laboratory for this work. Please do not report averages, but individual determinations only.

"In addition to reporting your results, will you please describe in detail the method or methods by which your results were obtained? Also please answer the following questions:

"*Moisture*.—(1) How much was weighed out for each determination? (2) At what temperature was the bath kept? (3) Was the sample dried for a specified number of hours, or to constant weight? (4) If the latter, approximately how long did it take to attain constant weight?

"*Nitrogen*.—(1) How much was weighed out for each determination? (2) In the Kjeldahl, Gunning or similar methods, approximately how long did it take for the solution to become clear or practically colorless? (3) How long after this occurred was digestion continued? (4) Was permanganate used? (5) Have you ever noticed evolution of chlorine when permanganate was added? (6) Was the entire digestion distilled, or an aliquot part, and if so, how much? (7) Approximately how long did the distillation last? (8) Approximately what volume was distilled off?

"It is desired to present as complete a report as possible at the Boston meeting, and the committee therefore asks that the results be sent within twenty days from receipt of samples and instructions."

Reports were received from forty-eight laboratories; many included the work of more than one analyst.

Determination of Moisture.—As the results came in it soon became evident that the determination of moisture, which was also asked for, presented at least as much, if not more difficulty than the nitrogen determination. Much stress was laid on this by many coöperators, as shown by the extensive and painstaking work reported upon, while many others seemed to attach no importance whatever to this feature.

Many reports included the results of a large number of determinations, often under different conditions and often also by different methods. In some cases an attempt was made to show differences in this way by means of single determinations. It is unfortunate, to say the least, that time and energy should be wasted in such attempts, instead of concentrating in one or two definite directions. Some reports included single determinations by one method only. The moisture determinations are summarized in Table 1.

TABLE 1.—DETERMINATION OF MOISTURE.—SUMMARY.

	Dried blood.	Tankage.	Complete fertilizer.
Number of individual determinations....	204	207	192
Number of individual averages.....	72	71	65
Mean of individual averages.....	6.15	1.56	1.83
Maximum of individual averages.....	7.74	2.49	2.99
Minimum of individual averages.....	5.07	0.89	1.07
Standard deviation.....	0.478	0.345	0.473
Probable error of the mean.....	0.0416	0.0292	0.0405
Probable error of the individual averages	0.330	0.230	0.319

A few sets of determinations by the vacuum method and one set by drying in hydrogen were received. A great many results were reported showing the effects of redrying and of drying under various conditions.

*In these cases only the results of the first drying were included in the averages as being deemed more nearly comparable with the results of drying but once, usually five hours. Aside from these repetitions, few results have been omitted from the averages. Only obviously erroneous results, shown to be so by subsequent work of the respective analysts themselves, were omitted. All the moisture results were

averaged together, because those reported by drying in vacuum were too few in number to furnish an average comparable with that obtained by drying with access of air.

There is a remarkable degree of variation between the various analysts. Atmospheric conditions such as of temperature or humidity appear to have at least as much, if not more, bearing on the results than variations in details of manipulation or drying. In one instance, it was possible to confirm this in the case of the dried blood, where a difference of 1 per cent. was obtained by two analysts in the same laboratory. The higher results were obtained during a wet snow-storm, while the lower were obtained on a bright, crisp, sunny, but cold day. Many series of determinations, on the other hand, showed clearly the effects of gradual absorption of moisture.

The means in Table 1 were calculated from the individual averages rather than from the individual single determinations, although in this way the results of single determinations were given equal weight with the results of duplicate and triplicate determinations. It is unfortunate that not all results were determined in duplicate or triplicate, but it is highly probable that any given number of determinations by a single analyst would give a less accurate and less desirable average than the same number of single determinations by as many analysts. Practically speaking, the former would represent just one set of accidental conditions of determinations, while the latter would represent a large and random assortment of sets of such accidental conditions.

The results summarized in Table 1 were also considered from a statistical standpoint and an attempt was made to find the measure of concentration of the determinations about the mean was made and expressed as the standard deviation in terms of per cent. of moisture. At the same time the probable error of the mean and of the individual average determinations were also calculated and these values are included in Table 1. It will be seen that these values are practically the same or very nearly the same order of magnitude for the three samples examined. The significance of these values will be discussed again further on in connection with the determination of nitrogen.

It will be seen from the above results that the determination of moisture, usually considered a very simple one, is in reality a very complex matter dependent upon conditions in a much larger measure perhaps than many other determinations or than is usually supposed to be the case.

Determination of Nitrogen.—The results of the determination of nitrogen have been grouped as far as possible according to the method employed. For the purposes of better comparison the average moisture values obtained by each analyst have been used in the nitrogen tables to calculate the results to a moisture-free basis. In cases where no moisture was determined the average moisture values from Table 1 were used for this purpose.

The result of the absolute or cupric oxid method follow in Table 2.

TABLE 2.—DETERMINATION OF NITROGEN. ABSOLUTE METHOD.

Anal.	Description of method.	Dried blood.				Tankage.				Complete fertilizer.			
		Nitrogen.				Nitrogen.				Nitrogen.			
		Per cent average moisture	Per cent indiv. determin.	Per cent mean	Per cent moisture free basis	Per cent average moisture	Per cent indiv. determin.	Per cent mean	Per cent moisture free basis	Per cent average moisture	Per cent indiv. determin.	Per cent mean	Per cent moisture free basis
1 B	Closed tube, without use of vacuum pump, CO ₂ from NaHCO ₃ . 0.15-0.25 gram taken for analysis.....
	Preliminary.....	16.37	11.88
	Final.....	16.43	11.55
		14.83
		15.22	9.95
		15.09	10.11
		15.28	10.07
		6.37	15.33	15.23	16.27	1.93	9.89	10.01	10.21
2	Open tube, specially long comb. tube, CO ₂ from NaHCO ₃ in special generator.....
	Preliminary.....	13.87	9.09	3.79
	Final.....	14.04	8.93
		14.68	9.18	4.17
		14.51	9.24	3.99
		6.46	...	14.60	15.61	1.51	9.35	9.24	9.38	2.02	3.99	4.05	4.13
3 B	Open tube, CO ₂ from conc. K ₂ CO ₃ sol. 0.16-0.53 gram taken for analysis.....	14.10	10.44	3.95
		6.34	13.93	14.02	14.97	1.46	10.44	10.44	10.59	1.91	4.17	4.06	4.14
17	Closed tube, CO ₂ from magnesite. 0.2-0.6 gram taken for analysis..	14.67	9.22	4.02
		6.10	14.70	14.69	15.63	1.27	9.20	9.21	9.35	1.51	3.95	3.99	4.05
		15.10	9.27	4.02
	Open tube, CO ₂ from NaHCO ₃	6.10	15.10	15.10	16.07	...	9.31	9.29	9.41	1.51	4.16	4.09	4.16
		14.96	9.55
18	Open tube.....	6.11	14.98	14.97	15.94	1.40	9.58	9.56	9.70	1.58	4.38	4.38	4.45

No attempt has been made to calculate averages from Table 2, as the results are too discordant. That the usual method of combustion is not adapted to this class of materials soon became evident to the analysts concerned. Analyst 2 in particular found that an unusually long time of combustion at a high heat was necessary to get off all the nitrogen, as shown in the difference between his preliminary and final results. It is not to be assumed that anything but nitrogen from the sample was measured in this work, but no explanation has been made of the great discrepancy of results obtained by this method, and we can only conclude that these materials are not adapted to the absolute method as usually carried out.

Only one set of results by the soda-lime method was received which is shown in Table 3.

TABLE 3.—DETERMINATION OF NITROGEN, SODA-LIME METHOD.

	Moisture. Per cent.	Nitrogen, moisture-free basis.	
		Per cent.	Per cent.
Dried blood.....	6.41	14.48	15.47
Tankage.....	1.33	9.61	9.74
Complete fertilizer.....	1.58	3.98	4.04

The excellent agreement of these results with those obtained by the "wet combustion" methods, as will be shown later, is all the more interesting, since only single determinations were made by this analyst. He states, however, that he has determined nitrogen by this method for sixteen years.

The results by the official Kjeldahl method have been divided into two sets. In Table 4 is shown a summary of the results where potassium permanganate was used to complete oxidation. The summary of the results by the same method without permanganate is shown in Table 5 and the results

by the other "wet combustion" methods are summarized in Tables 6-10.

TABLE 4.—DETERMINATION OF NITROGEN. KJELDAHL METHOD WITH PERMANGANATE.

	No. of analysts.	No. of indiv. determination.	Nitrogen.				
			Moist	Mean	Maximum	Minimum	Mean, moisture-free basis.
Dried blood.....	27	77	6.13	14.39	14.56	14.11	15.32
Tankage.....	27	81	1.56	9.57	9.80	9.37	9.72
Complete fertilizer....	27	74	1.77	4.06	4.15	3.90	4.13

The results of one analyst only were omitted from Table 4 as they were abnormally high. No explanation could be found for this and although it seems probable that the fault lay with the standard acid and alkali employed, this opinion is purely speculation.

As the results of one analyst are of particular interest in the case of the dried blood and the tankage, indicating a definite tendency towards higher results with increased time of digestion, they have been tabulated together with his results by the Gunning method in Table 8. An attempt to show this tendency was also made by one or two other analysts, although not so clearly and successfully.

TABLE 5.—DETERMINATION OF NITROGEN. KJELDAHL METHOD WITHOUT PERMANGANATE.

	No. of analysts.	No. of indiv. determination.	Nitrogen.				
			Moist	Mean	Maximum	Minimum	Mean, moisture-free basis.
Dried blood.....	10	23	5.81	14.39	14.54	14.29	15.30
Tankage.....	10	32	1.63	9.51	9.59	9.32	9.66
Complete fertilizer....	10	25	1.95	4.05	4.17	3.92	4.13

A comparison of the individual results by the Kjeldahl method shows a general tendency towards shortening the time of digestion where permanganate was used. On the other hand, the agreement of the results with permanganate is not quite so good as that of the results where permanganate was omitted. It is natural to draw the inference that the use of permanganate does not seem to be a perfectly satisfactory substitute for longer digestion.

TABLE 6.—DETERMINATION OF NITROGEN. KJELDAHL-GUNNING METHOD WITH PERMANGANATE.

	No. of analysts.	No. of indiv. de-termination.	Nitrogen.				Mean, moisture-free basis.
			Moist.	Mean.	Maximum.	Minimum.	
Dried blood.....	5	13	6.15	14.41	14.51	14.33	15.36
Tankage.....	5	14	1.48	9.53	9.66	9.39	9.67
Complete fertilizer....	5	11	2.01	4.02	4.12	3.89	4.10

This table includes a few results obtained with potassium sulphate in addition to mercury and permanganate. The results in this table indicate that this method will yield results agreeing very well with those in Tables 4 and 5, although the time of digestion may be extremely short.

TABLE 7. DETERMINATION OF NITROGEN. GUNNING METHOD

	No. of analysts.	No. of indiv. de-termination.	Nitrogen.				Mean, moisture-free basis.
			Moist.	Mean.	Maximum.	Minimum.	
Dried blood.....	15	50	6.25	14.37	14.56	14.26	15.32
Tankage.....	15	42	1.65	9.48	9.66	9.39	9.63
Complete fertilizer....	15	38	1.95	4.06	4.16	3.90	4.13

The individual results in Table 7 indicate that while a short time of digestion in the Gunning method may not necessarily cause low results yet low results are

TABLE 8.—DETERMINATION OF NITROGEN. 1. KJELDAHL METHOD WITH PERMANGANATE. 2. GUNNING METHOD

Total time of diges- tion.	Dried blood.					Tankage.					Complete fertilizer.				
	Nitrogen.				Per cent. mois- ture-free basis.	Nitrogen.				Per cent. mois- ture-free basis.	Nitrogen.				Per cent. mois- ture-free basis.
	Per cent. aver- age moisture.	Per cent. indiv. de- termination.	Per cent. mean.			Per cent. aver- age moisture.	Per cent. indiv. de- termination.	Per cent. mean.			Per cent. aver- age moisture.	Per cent. indiv. de- termination.	Mean mois- ture		
1 Until clear.....	..	14.34	9.54
2-3 hours.....	..	14.38	9.59
..	..	14.43	9.53	4.08
..	..	14.48	9.55	4.09	4.09	4.15	..
2½ hrs. after clearing.....	..	14.37	9.48
3½ hrs. after clearing.....	..	14.53	9.30
4½ hrs. after clearing.....	6.11	14.55	14.43	15.37	..	1.40	9.44
2 Until clear.....	..	14.32	9.51	9.49	9.63	1.58
2-3 hours.....	..	14.37	9.56	4.06
..	..	14.43	9.64	4.05
..	..	14.43	9.61	1.58	4.09	4.07	4.13	..
..	..	14.43	9.65
2-2½ hrs. longer.....	..	14.42	9.58
3-3¾ hrs. longer.....	..	14.58	9.44
4-4½ hrs. longer.....	6.11	14.60	14.45	15.39	..	1.40	9.46
..	9.60	9.57	9.71

practically always accompanied by a short time of digestion. The inference is that the time of digestion in the Gunning method must be longer than in any other "wet combustion" method, probably not less

than four to five hours. This has been confirmed by the work of Sherman and Falk.¹

The low results of several analysts in the case of the dried blood would seem to indicate clearly too short a time of digestion. The analyst referred to previously on the other hand, again demonstrates very clearly the tendency of increased time of digestion towards higher results and his results by the Gunning and by the Kjeldahl method are shown in Table 8.

TABLE 9.—DETERMINATION OF NITROGEN. KJELDAHL-GUNNING METHOD

	No. of analysts.	No. of indiv. de-termination.	Nitrogen.				Mean, moisture-free basis.
			Moist.	Mean.	Maximum.	Minimum.	
Dried blood.....	23	59	6.29	14.47	14.66	14.26	15.44
Tankage.....	23	58	1.67	9.65	9.80	9.41	9.81
Complete fertilizer....	23	58	2.04	4.10	4.21	3.76	4.18

This method, involving the use of both potassium sulphate and mercury, is being used widely outside of official fertilizer control and is also apparently in considerable use for fertilizer control work in the laboratories of fertilizer manufacturers. It shows a distinct tendency towards higher results, and the agreement between the various analysts is perhaps somewhat better than that obtained by the other "wet combustion" methods, since no results had to be omitted from this table.

TABLE 10. DETERMINATION OF NITROGEN. GUNNING METHOD WITH COPPER SULPHATE

	No. of analysts.	No. of indiv. de-termination.	Nitrogen.				Mean, moisture-free basis.
			Moist.	Mean.	Maximum.	Minimum.	
Dried blood.....	7	21	5.85	14.42	14.65	14.24	15.38
Tankage.....	7	21	2.26	9.51	9.70	9.39	9.69
Complete fertilizer....	7	18	1.84	4.06	4.17	3.94	4.13

A similar tendency towards higher results, though not so marked as in the Kjeldahl-Gunning method is shown in the results by the Gunning method with

¹ J. Am. Chem. Soc., 26, 1469 (1904).

copper sulphate which has recently been adopted as official by the A. O. A. C.

TABLE 11. DETERMINATION OF NITROGEN. KJELDAHL METHOD, 9 TO 11. COPPER SULPHATE.

	No. of analyses	No. of indiv. determinations	Nitrogen			
			Moist	Mean	Maximum	Minimum
Dried blood	2	10	5.17	14.44	14.48	14.41
Tankage	2	10	1.11	9.55	9.88	9.88
Complete fertilizer	2	10	1.44	4.07	4.09	4.08

The results by this method are too few in number to afford a satisfactory basis for comparison with other methods. From the results reported, however, no particular advantage is evident from the use of both copper sulphate and mercury.

Attention is also called in this connection to the recent work of Hibbard on the use of copper sulphate.¹ The average results of all the "wet combustion" methods tabulated above are given in the following table.

This table shows very clearly in the case of the dried blood that the lowest results were obtained by the Kjeldahl method with and without permanganate and by the Gunning method, while the highest results were obtained by the Kjeldahl-Gunning method. This is also true in the case of the tankage, except in the Kjeldahl method with permanganate and is also true, though to a lesser degree, in the case of the complete fertilizer. The use of copper sulphate as shown in Tables 9 and 10 also tends towards slightly higher results, but not quite so much as the use of potassium sulphate with mercury, *i. e.*, the Kjeldahl-Gunning method.

Table 9 could be duplicated by other analysts than those who were accustomed to using this method, requests for further work were sent out by the chairman of the committee to a number of analysts who had not reported results by this method, together with the following letter of instructions.

"I am enclosing a tabulation of the range and averages of results obtained on the three standard samples sent out by the Committee on Nitrogen and I should be glad to have your comments after you have looked over these results.

"If you have sufficient of the samples left, will you kindly retest these in triplicate by the following method and report to me within thirty days? If you have not enough left, please notify me at once.

Determination of Moisture and Nitrogen.—When weighing, the entire contents of each bottle should be spread on a sheet of glazed paper and after mixing well, the portions for the determination of moisture as well as for nitrogen should be taken at the same time from the sample thus spread out, mixing again after each weighing, so as to obtain truly representative portions.

Moisture.—Weigh out, in triplicate, portions of approximately 2.5 grams into weighing dishes which can be tightly covered or watch-glasses held together by clips in the usual manner.

"Do not try to weigh out exactly 2.5 grams, but after having placed approximately 2.5 grams in the dish, cover tightly and finish weighing. Dry for four hours, keeping the temperature of the bath as close to 100° C. as possible. The ventilation of the bath should be as efficient as it can possibly be made. Cool in tightly covered dishes in the desiccator for one hour before weighing.

Nitrogen.—Weigh on a nitrogen-free filter paper

TABLE 12.—DETERMINATION OF NITROGEN. GENERAL MEAN VALUES FROM TABLES 4 TO 7

Table	Method.	Dried blood.				Tankage.				Complete fertilizer.			
		Per cent. average moisture.	Per cent. indiv. determination	Per cent. mean.	Per cent. moisture free basis.	Per cent. average moisture.	Per cent. indiv. determination	Per cent. mean.	Per cent. moisture free basis.	Per cent. average moisture.	Per cent. indiv. determination	Per cent. mean.	Per cent. moisture free basis.
4	Kjeldahl with permanganate	6.13	14.38	14.39	15.32	1.56	9.57	9.57	9.72	1.77	4.08	4.06	4.13
5	Kjeldahl without permanganate	5.81	14.37	14.39	15.30	1.63	9.45	9.51	9.66	1.95	4.03	4.05	4.13
6	Kjeldahl-Gunning with permanganate	6.15	14.38	14.41	15.36	1.48	9.52	9.83	9.67	2.01	4.02	4.02	4.10
7	Gunning	6.25	14.38	14.37	15.32	1.65	9.48	9.48	9.63	1.95	4.06	4.06	4.13
8	Kjeldahl-Gunning	6.29	14.47	14.47	15.44	1.67	9.65	9.81	9.81	2.04	4.03	4.10	4.18
9	Gunning with copper sulphate	5.85	14.48	14.42	15.38	2.26	9.54	9.81	9.69	1.84	4.08	4.06	4.13
10	Kjeldahl with copper sulphate	5.17	14.46	14.44	15.23	1.11	9.88	9.88	9.66	1.44	4.06	4.07	4.16

In general, however, the agreement of the corresponding nitrogen values from all the tables must be considered quite satisfactory, whether considered as determined or on a moisture-free basis. The greatest variation is shown in the case of the dried blood in Table 11 on a moisture-free basis, but this is due to the coincidence that the only two analysts reporting this method obtained a much lower moisture value than the average.

In order to determine whether the high results obtained by the Kjeldahl-Gunning method as shown in

(an ash-free 11 cm. filter paper answers this requirement) 1.401 grams of the blood and of the tankage and 2.802 grams of the mixed fertilizer. Also weigh out three portions of 2 grams each of pure sugar in the same manner. To each of these weighed portions add 5 grams of potassium sulphate and 0.7 gram of mercuric oxide (0.5 gram of pure mercury may be substituted for the mercuric oxide).

"Roll up each weighed portion in its filter paper and drop it into the digestion flask, then add 25 cc. of concentrated sulphuric acid and digest, noting approximately the time it takes for the contents to be-

¹ THIS JOURNAL, 2, 463 (1910).

come (a) entirely liquefied, and (b) to become colorless or practically so. Digestion should be continued for two hours after final color has been reached. The general experience with this method has been that the digestion comes to final color in 30-45 minutes and the total digestion can, therefore, be made in from two to two and one-quarter hours.

"Do not use permanganate, but distil the entire digestion. After cooling, dilute with 200 cc. of water, add a little granulated zinc and then a mixture of 25 cc. of a 4 per cent. potassium sulphide solution with the necessary quantity of caustic soda solution. Distil off not less than 200 and not more than 250 cc. Determine the ammonia in the distillate in the usual manner, using cochineal as indicator. Report results as both ammonia and nitrogen, giving your individual results and blanks, not averages."

At the same time a tentative tabulation of the averages obtained up to that time was sent to all coöperators, and in considering the results of this additional work as summarized in Tables 13 and 14, it must be borne in mind that the results of the previous work were known in a general way by those in charge of the various laboratories, if not by analysts actually doing the work, thus affording opportunity for revision where desired.

TABLE 13.—DETERMINATION OF MOISTURE. METHOD AS OUTLINED BY COMMITTEE ON NITROGEN.

	No. of analysts.	No. of indiv. termination.	Moisture.		
			Mean.	Maximum.	Minimum.
Dried blood.....	12	40	6.57	7.82	5.07
Tankage.....	12	38	2.38	4.73	1.06
Complete fertilizer.....	12	36	2.42	3.51	1.62

These results show a larger variation than the values given in Table 1 and indicate that in many cases considerable moisture had been absorbed by the samples in the meantime. Some of the results shown in this table were obtained on the remainder of the original samples in the possession of the respective analysts, others were obtained on fresh samples supplied by the committee. For this reason a statistical treatment of the results was not attempted.

Criticism was freely made on that part of the direc-

tions which specify that the samples were to be spread out on a glazed paper and thoroughly mixed after the withdrawal of each portion weighed out. This criticism is well founded, particularly if the determinations are made on days when the relative humidity is high and will have to be taken into consideration in formulating methods for future work on this subject. It will have to be remembered, however, that these materials are not homogeneous, that it is not feasible in control work to weigh out other than a factor weight, so as to avoid unnecessary calculation and that the resulting tendency to unmix must be overcome. It is easily possible for instance, either intentionally or carelessly, to weigh portions of dried blood from the same sample which will differ from each other by 0.5 per cent. of nitrogen or more.

The results of the nitrogen determinations are summarized in Table 14.

TABLE 14.—DETERMINATION OF NITROGEN. KJELDAHL-GUNNING METHOD AS OUTLINED BY COMMITTEE ON NITROGEN.

	No. of analysts.	No. of indiv. termination.	Moist.	Nitrogen.			Mean moist-free basis.
				Mean.	Maximum.	Minimum.	
Dried blood.....	16	58	6.62	14.37	14.56	14.05	15.41
Tankage.....	16	61	2.58	9.51	9.78	9.02	9.76
Complete fertilizer.....	16	39	2.41	4.09	4.17	4.00	4.19

The individual results summarized above show no improvement in agreement between the various analysts over the previous tables. The averages of the nitrogen results as determined are lower than the averages in Table 9, but this is obviously due to the absorption of moisture by many of the samples reported upon in this table. When, however, the averages on a moisture-free basis are considered, it will be seen that the tendency towards higher average results shown in Table 9 is confirmed. This is shown very clearly in Table 15, which is essentially the same as Table 12 with the data from Tables 13, 14 and 3 added.

In order to show whether the results by any of the methods were more uniform than those obtained by other methods, a comparison of the statistical data calculated from the various tables is given in Table 16.

TABLE 15.—DETERMINATION OF NITROGEN. GENERAL MEAN VALUES FROM TABLES 3, 4 TO 10 AND 14.

Table.	Method.	Dried blood.				Tankage.				Complete fertilizer.			
		Nitrogen.			Per cent. moisture-free basis.	Nitrogen.			Per cent. moisture-free basis.	Nitrogen.			Per cent. moisture-free basis.
		Per cent. average moisture.	Per cent. indiv. determination.	Per cent. mean.		Per cent. average moisture.	Per cent. indiv. determination.	Per cent. mean.		Per cent. average moisture.	Per cent. indiv. determination.	Per cent. mean.	
3	Soda lime.....	6.41	14.48	...	15.47	1.33	9.61	...	9.74	1.58	3.98	...	4.04
4	Kjeldahl with permanganate.....	6.13	14.38	14.39	15.32	1.56	9.57	9.57	9.72	1.77	4.05	4.06	4.13
5	Kjeldahl without permanganate.....	5.81	14.37	14.39	15.30	1.63	9.45	9.51	9.66	1.95	4.03	4.05	4.13
6	Kjeldahl-Gunning with permanganate.....	6.15	14.38	14.41	15.36	1.48	9.52	9.53	9.67	2.01	4.02	4.02	4.10
7	Gunning.....	6.25	14.38	14.37	15.32	1.65	9.48	9.48	9.63	1.95	4.06	4.06	4.13
8	Kjeldahl-Gunning.....	6.29	14.47	14.47	15.44	1.67	9.65	9.81	9.81	2.04	4.03	4.10	4.18
9	Gunning with copper sulphate.....	5.85	14.48	14.42	15.38	2.26	9.54	9.51	9.69	1.84	4.08	4.06	4.13
10	Kjeldahl with copper sulphate.....	5.17	14.46	14.44	15.23	1.11	9.55	9.55	9.66	1.44	4.06	4.07	4.16
14	Kjeldahl-Gunning as outlined by the committee.....	6.62	14.37	14.37	15.41	2.58	9.52	9.51	9.76	2.41	4.09	4.09	4.19

TABLE 16.—COMPARATIVE STATISTICAL DATA FROM TABLE I

Table.	Method.	Dried blood			Tannage			Single fertilizer		
		Per cent standard deviation	Per cent probable error of the mean	Per cent probable error of a single determination	Per cent deviation	Per cent probable error of the mean	Per cent probable error of a single determination	Per cent standard deviation	Per cent probable error of the mean	Per cent probable error of a single determination
1	Moisture.....	0.478	0.0416	0.330	0.345	0.0292	0.230	0.473	0.0405	0.319
4	Kjeldahl with permanganate.....	0.142	0.019	0.096	0.108	0.014	0.073	0.062	0.008	0.041
5	Kjeldahl without permanganate.....	0.104	0.0266	0.070	0.140	0.0357	0.0946	0.0864	0.0238	0.0583
6	Kjeldahl-Gunning with permanganate.....	0.074	0.022	0.050	0.115	0.035	0.078	0.094	0.028	0.064
7	Gunning.....	0.119	0.022	0.080	0.107	0.019	0.073	0.053	0.012	0.036
8	Kjeldahl-Gunning.....	0.127	0.028	0.086	0.114	0.025	0.077	0.0828	0.018	0.056
9	Gunning with copper sulphate.....	0.167	0.0033	0.142	0.109	0.0088	0.074	0.091	0.0079	0.061
14	Kjeldahl-Gunning.....	0.122	0.0178	0.082	0.118	0.0194	0.080	0.046	0.0083	0.031

The agreement of the various analysts on moisture determinations is shown clearly to be decidedly inferior to the agreement on nitrogen determinations. Moreover, it was not possible to show any degree whatever of correlation between the corresponding moisture and nitrogen determinations. It was to be expected, for instance, that low nitrogen values on the part of any one analyst would be accompanied by correspondingly high moisture values, but no relation of this sort could be demonstrated.

Practically all the corresponding nitrogen data are of the same order of magnitude, and the exceptions are either confined to tables with comparatively few results, or they are of nearly the same order of magnitude as the majority of the data.

The committee does not, therefore, deem it expedient to make recommendations in favor of any particular method. As a matter of fact, it became evident during the progress of the work that the standardization of the samples prepared would ultimately prove to be of more value than any other feature of the work. There is a considerable supply of the samples of dried blood and tannage available. The supply of complete fertilizer has been exhausted, as only a limited number of samples of this material were prepared for the purpose of showing that greater uniformity would be obtainable among different analysts in the case of a material of low nitrogen content than in one of high nitrogen content. A study of the results of this work fully confirms this view, which was, moreover, to be expected from a purely mathematical standpoint.

The data brought out by the questions included in the letter of instructions were not all tabulated.

The arrangement of the tables shows whether permanganate was or was not used in any given case.

The amount weighed out for the determination of nitrogen was very uniform, between 1 and 2 grams.

The time of digestion to colorless, light straw or straw-yellow was variously given as from twenty minutes to three hours, usually from one-half to one and one-half hours. The total time of digestion varied from one to four hours.

No evolution of chlorine was noticed by any one but the analyst who raised the question.

Only eight analysts took aliquot parts of the digestion for distillation. In all other cases the entire digestion was distilled.

The time of distillation and the volume distilled off, where stated, varied considerably and no definite tendency could be observed in a study of the data obtained on these points.

The standard acid and alkali constitute a very important factor in this work. Comparative tests were made by one of the members of the committee with five of the coöperating analysts. In four of these cases the agreement was most excellent, while in the fifth there was a difference, but not sufficient to account for the materially higher results obtained by this particular analyst. Since, however, differences in this respect may become cumulative together with differences from other sources, the committee believes that this phase of the subject requires further study.

The results of this work may be summarized as follows:

First.—Results were reported by forty-eight coöperating laboratories.

Second.—An average of over 220 individual moisture determinations on each of the three samples were received and tabulated.

Third.—The agreement obtained between the results of moisture determinations of the coöperating analysts was much inferior to that obtained in the determination of nitrogen.

Fourth.—In future coöperative work on the determination of moisture, atmospheric conditions will have to be taken into consideration in addition to details of manipulation, apparatus and methods of drying.

Fifth.—Special precautions are necessary in the preparation and packing of samples representing shipments of these and similar commodities in order that changes in the moisture content may be reduced to a minimum.

Sixth.—An average of over 250 individual nitrogen determinations on each of the three samples were received and tabulated.

Seventh.—The absolute or cupric oxid method as usually carried out does not appear to be applicable to dried blood or tannage.

Eighth.—Since only one set of single determinations by the soda-lime method was received, no conclusions can be drawn or comparisons made between this and other methods which would be general in their nature.

Ninth.—The "wet combustion" methods give mean values which agree satisfactorily with each other,

whether these values be considered as determined or whether they be calculated to a moisture-free basis.

Tenth.—The Kjeldahl-Gunning method, *i. e.*, the use of potassium sulphate with mercury, gives consistently higher mean results than any other wet combustion method.

Eleventh.—Since the chances for error in the "wet combustion" method, aside from possible errors in standard acid and alkali, rarely, if ever, tend towards high results, it is safe to assume that the mean of the Kjeldahl-Gunning method gives more nearly the true nitrogen content than the other "wet combustion" methods. The only common sources of error in determining nitrogen by "wet combustion" which would tend towards high results would be contamination with ammonia fumes either during digestion or distillation and the driving over of caustic alkali during distillation as sometimes happen when too great an excess of alkali is used and the contents of the distilling flasks are boiled down too far or when foaming occurs unnoticed. Practically all other ordinary sources of error would tend towards low results, aside from errors in the standard solutions used.

Twelfth.—The Gunning method apparently requires a longer time of digestion than the other "wet combustion" methods. If the total time of digestion in this method is less than four hours, there is danger of low results.

Thirteenth.—In the Kjeldahl method, permanganate apparently enables the operator to shorten the time of digestion, but the use of permanganate is objectionable to many analysts and is unnecessary, if either a longer time of digestion or the use of potassium sulphate in conjunction with mercury (Kjeldahl-Gunning method) be employed.

Fourteenth.—The use of copper sulphate does not appear to represent any advantages over the use of mercury in point of time of digestion, its chief advantage consisting in doing away with the use of sulphid.

The committee is of the opinion that the very large number of individual determinations reported in this work may be safely assumed to form a good basis for approximating the true nitrogen content of the samples in question within narrow limits so far as shown by the "wet combustion" methods. Indeed, for practical purposes and from a commercial standpoint, it may be safely assumed that the true nitrogen values of these samples have been obtained with a satisfactory degree of accuracy, provided that analysts availing themselves of these samples will not attempt to determine the nitrogen without also carefully determining the moisture at the same time.¹

The committee desires to acknowledge its indebtedness to all those who coöperated in this work, and to thank them for the cordial spirit with which our requests were met throughout the work. Special acknowledgment is due to Dr. H. S. Grindley and

Mr. H. H. Mitchell, of the University of Illinois, for their valuable advice and assistance in the statistical study of the numerical results of this work.

Among those who coöperated in this work were the following:

F. G. Allison, College of Agriculture, University of Illinois, Urbana, Ill.

B. W. Bangs, American Agricultural Chemical Company, Carteret, N. J.

G. F. Beyer, Armour & Company, So. Omaha, Neb.

J. E. Breckenridge, American Agricultural Chemical Company, Carteret, N. J.

Dr. J. S. Burd, University of California, Berkeley, California.

L. M. Burghardt, University of Illinois, Urbana, Illinois.

L. S. Bushnell, Armour & Company, Kansas City, Kansas.

Dr. F. B. Carpenter, Virginia-Carolina Chemical Company, Richmond, Va.

E. Carroll, University of Illinois, Urbana, Illinois.

Professor Cavanaugh, Cornell University, Ithaca, New York.

Paul Collins, New Haven, Conn.

W. D. Cooke, Virginia-Carolina Chemical Company, Richmond, Va.

Dr. C. E. Derick, University of Illinois, Urbana, Illinois.

W. P. Dunne, Morris & Company, Chicago, Illinois.

G. Farnham, Jarecki Chemical Company, Cincinnati, Ohio.

Frederick Fenger, Armour & Company, Chicago, Illinois.

T. B. Ford, Bureau of Standards, Washington, D. C.

Gascoyne & Company, Baltimore, Md.

F. W. Gill, College of Agriculture, University of Illinois, Urbana, Ill.

Geo. Guckenberger, F. C. Broeman & Company, Cincinnati, Ohio.

H. H. Hanson, Maine Agr. Exp. Station, Orono, Maine.

Dr. B. L. Hartwell, Rhode Island Agr. Exp. Station, Kingston, R. I.

P. L. Hibbard, University of California, Berkeley, California.

T. N. Havlin, Morris & Company, E. St. Louis.

O. C. Haworth, Lafayette, Indiana.

C. C. James, Pacific Guano & Fertilizer Company, Honolulu, H. T.

C. H. Jones, Vermont Agr. Exp. Station, Burlington, Vermont.

W. J. Jones, Jr., Indiana State Chemist, Lafayette, Indiana.

Dr. G. E. F. Lundell, Cornell University, Ithaca, New York.

Wilson H. Low, Cudahy Packing Company, So. Omaha, Neb.

A. Lowenstein, Morris & Company, Chicago, Illinois.

Dr. F. J. Maywald, 89 Pine Street, New York.

McCandless Laboratory, Atlanta, Ga.

P. L. McCreary, University of California, Berkeley, California.

¹ For the present, further samples may be obtained upon application to the chairman of this committee, and inasmuch as no funds are available for this purpose, applicants for these samples are requested to remit \$0.15 for each sample desired to cover postage and packing.

Dr. A. T. McLeod, University of Chicago, Chicago, Illinois.

W. D. McNally, Armour & Company, National Stock Yards, Illinois.

G. W. Miles, Boston, Mass.

W. C. Moor, Armour & Company, North Ft. Worth, Texas.

E. G. Moore, Morris & Company, Chicago, Illinois.

H. C. Moore, Armour Fertilizer Works, Atlanta, Ga.

F. A. Nantz, Arkansas Cotton Oil Company, Little Rock, Arkansas.

Rudolph Neu, Armour Fertilizer Works, Jacksonville, Florida.

P. K. Nisbet, American Agricultural Chemical Co., No. Weymouth, Mass.

Dr. F. L. Parker, Jr., Parker Laboratory, Charleston, S. C.

C. L. Pfersch, New Jersey Agr. Exp. Station, New Brunswick, New Jersey.

J. R. Powell, Armour Glue Works, Chicago, Illinois.

E. G. Proulx, Lafayette, Indiana.

W. D. Richardson, Swift & Company, Chicago, Illinois.

W. Rodes, Kentucky Agr. Exp. Station, Lexington, Kentucky.

F. Roman, University of Illinois, Urbana, Illinois.

I. R. Rothrock, Armour Fertilizer Works, Baltimore, Md.

Paul Rudnick, Armour & Company, Chicago, Illinois.

O. M. Shedd, Kentucky Agr. Exp. Station, Lexington, Kentucky.

S. H. Sheib, Tennessee Chemical Company, Nashville, Tennessee.

John Short, E. Rauh & Sons, Fertilizer Company, Indianapolis, Ind.

Professor J. F. Snell, McDonald College, Quebec, Canada.

H. D. Spears, Kentucky Agr. Exp. Station, Lexington, Kentucky.

B. E. St. John, Morris & Company, Kansas City.

E. E. Thomas, University of California, Whittier, California.

E. O. Thomas, Norfolk, Va.

T. C. Trescot, Bureau of Chemistry, Washington, D. C.

W. L. Whitehouse, Coe-Mortimer Company, Moosic, Pa.

Dr. T. J. Willard, Kansas Agr. Exp. Station, Manhattan Kansas.

Dr. F. W. Woll, University of Wisconsin, Madison, Wisconsin.

Respectfully submitted,

Committee on Nitrogen,

C. H. JONES,

F. C. ATKINSON,

F. L. PARKER, JR.,

PAUL RUDNICK, *Chairman*.

While the laws are ample to protect both the manufacturers and consumers, there is a tendency among a certain class of representatives from the rural districts to introduce bills in the Legislatures which if enacted would impose useless hardships upon the manufacturers and would afford practically no additional protection to the consumers. Fortunately the "rule of reason" usually prevails, and not many of these proposed regulations are enacted into laws. Such bills as I refer to if they should become laws would necessarily increase the price of fertilizers to the consumers. It is, therefore, for the best interests of all concerned to endeavor as far as possible to encourage the passage of such laws as will protect all interests concerned, and impose the least hardship on the manufacturer.

The matter of most importance at the present time is the examination of fertilizers for the availability of the organic nitrogen contained. The different agricultural departments have taken up this matter and adopted tentative methods of analysis which have been in force during the past season. The New England States, including New York and New Jersey, are using what is known as the alkaline permanganate method, and the Southern States the neutral permanganate with final recourse to the pepsin hydrochloric acid method. It is a well known fact that none of these methods will give satisfactory results on all classes of materials, and the results on the same materials by the different methods are entirely at variance. It is to be hoped that before any method is enacted into a law a more satisfactory process will be devised which will not only give the true value of the different classes of ammoniates, but will give uniform and satisfactory results in the hands of different analysts.

F. B. CARPENTER,

Chairman.

POTASH WORK OF FERTILIZER DIVISION WITH COMPARISON OF OFFICIAL METHOD AS GIVEN IN BULLETIN, 1907, U. S. DEPARTMENT OF AGRICULTURE AND A MODIFIED METHOD.

JUNE MEETING, A. C. S., 1911.

Modified official method which consisted in washing two grams on eleven cm. filter paper with small portions of hot (boiling) water into a 200 cc. flask to about 175 cc., adding two cc. concentrated HCl-Am. and ammonium oxalate and proceeding as in Official Method. Moisture determinations were also asked.

Forty-two samples were sent out and twenty-three replies received. Those taking part in the work were:

P. L. McCreary, University of California, Berkeley, Cal.

P. L. Hibbard, University of California, Berkeley, Cal.

J. S. Burd, University of California, Berkeley, Cal.

W. D. McNally, Armour & Co., E. St. Louis, Ill.

F. N. Smalley, S. C. O. Co., Savannah, Ga.

W. C. Dumas, Lloyd Laboratory, Atlanta, Ga.

F. B. Porter, Swift & Co., Atlanta, Ga.

REPORT OF COMMITTEE ON FERTILIZER LEGISLATION.

JUNE MEETING, A. C. S., 1911.

There has been no material change in the fertilizer laws of the different states since our last meeting.

F. B. Carpenter, V.-C. C. Co., Richmond, Va.
 J. P. Street, Ct. Agr. Exp. Station, New Haven, Ct.
 C. B. Morrison, Ct. Agr. Exp. Station, New Haven, Ct.
 R. B. Roe, Ct. Agr. Exp. Station, New Haven, Ct.
 C. A. Butts, 702-3 Forsyth Bldg., Atlanta, Ga.
 H. B. Battle, Montgomery, Ala.
 McCandless Laboratory, Atlanta, Ga.
 C. H. Jones, Vt. Agr. Exp. Station, Burlington, Vt.
 W. B. Derby, Vt. Agr. Exp. Station, Burlington, Vt.
 E. P. Verner, Parker Laboratory, Charleston, S. C.
 F. A. Nantz, N. O. Acid & Fert. Co., New Orleans, La.
 B. W. Bangs, Am. Agr. Chem. Co., Carteret, N. J.
 J. E. Breckenridge, Am. Agr. Chem. Co., Carteret, N. J.
 M. H. Pingree, Am. Agr. Chem. Co., Baltimore, Md.
 P. K. Nisbet, Am. Agr. Chem. Co., North Weymouth, Mass.
 G. A. Farnham, Jarecki Chem. Co., Cincinnati, O.
 L. W. Thurbow, Great Western Sugar Co., Loveland, Colo.
 W. H. Whitehouse, Coe Mortimer Co., Moosic, Pa.
 P. Rudnick, Armour & Co., Chicago, Ill.
 Names are not in order of number of analyst used in report.

Results were as follows:

Analyst.	Potash official.		Mod. off.		Dif. in favor of mod. off.
	No. 1.	No. 2.	No. 3.	No. 4.	
1	..	7.81	..	8.30	0.49
2	7.04	..	7.62
	7.06	7.05	7.58	7.60	0.55
3	..	7.14	..	7.53	0.39
4	..	7.08	..	7.49	0.41
5	..	7.38	..	7.67	0.29
6	..	7.17	..	7.32	0.15
7	..	7.38	..	8.07	0.69
8	7.42	..	8.01
	7.31	..	8.76
	7.42	7.38	7.95	7.94	0.56
9	7.74	..	8.18
	7.74	..	8.20
	7.70	..	8.16
	7.74	7.73	8.16	8.18	0.45
10	..	7.47	..	8.02	0.45
11	..	7.40	..	8.33	0.93
12	..	7.74	..	7.85	0.11
13	..	7.33	..	7.22	..
14	..	7.90	..	7.98	..
15	7.05	..	7.88
	7.15	..	7.78
	7.08	7.09	7.90	7.85	0.76
16	..	7.67	..	8.09	0.42
17	..	6.59	..	7.12	0.53
18	..	7.72	..	8.24	0.48
19	..	7.64	..	8.22	0.58
20	..	6.78	..	7.21	0.43
	..	6.82	..	7.25	0.43
21	..	6.69	..	7.07	0.38
22	..	7.40	..	7.72	0.32
	..	7.32	..	7.80	0.48
23	..	7.41	..	7.79	0.38
	..	7.40	..	7.77	0.37
	..	7.44	..	7.80	0.36
24	..	7.26	..	7.82	0.56

Average + difference in favor of Modified Official Method, 0.45 per cent.

Moisture determinations were reported at temperatures from 98° to 130°.

Those made at 98-100° were from 3.65 to 5.18. Five hours seemed to be sufficient time to reach constant weight.

Sample contained large percentage of iron and aluminum phosphate, about eight per cent. iron and aluminum oxides, was ground to No. 30 mesh screen and thoroughly mixed. Theoretical amount of potash added was 8.30 per cent. in form of muriate.

Conclusions: Modified Official Method gave average increase in potash soluble in water of 0.45 per cent.

No. 1 and No. 3 column individual determinations, No. 2 and No. 4 averages.

AMERICAN ELECTROCHEMICAL SOCIETY.

The 20th general meeting of the Society will be held in Toronto, Canada, September 21-23, 1911. The preliminary program as far as outlined at this writing is as follows, subject to revision:

THURSDAY, SEPTEMBER 21ST.

Morning Session.

Reading and discussion of papers.

Afternoon Session.

Reading and discussion of papers.

Evening.

Meeting of Board of Directors, followed by smoker and entertainment by Section Q.

FRIDAY, SEPTEMBER 22ND.

Morning Session.

(Probably at some golf club) reading and discussion of papers.

Afternoon.

Golf tournament, etc.

Evening.

Banquet at McConkey's Restaurant.

SATURDAY, SEPTEMBER 23RD.

Morning.

Visit to Canadian General Electric Company's Plant at Peterboro. Return trip through locks to reach town in time to catch 5 P.M. boat out of town.

Members are requested to fill out and mail the cards enclosed in June Bulletin signifying their intention of attending the 20th general meeting, so that the Local Committee can make proper arrangements for their entertainment.

Members having papers to present at this meeting should notify either Chairman Lidbury, of the Papers Committee, or the Secretary before September 1st, sending titles of same so as to secure a place on the program.

W. S. LANDIS, *Assistant Secretary.*

LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.,
 August 10, 1911.

THE TRAINING OF INDUSTRIAL CHEMISTS IN ENGLAND.

At the annual meeting of the Society of Chemical Industry, held in Sheffield in July, the president, in his address, said that new apparatus, methods, and products appeared with such rapidity that it had become extremely difficult to keep pace with all the applications of science to industry. The tendency of the present age was toward specialization, but too minute subdivision had its disadvantages. There would always, therefore, be a demand for trained men who

had a good knowledge of science generally, and especially of the methods of applying it. It was sometimes alleged that the nature of the training given to students in this country was not practical enough, and that some foreign nations were superior to us in this respect. He did not think the facilities for acquiring knowledge were less in Great Britain than in any other country—in fact, in some of our institutions they were superior—but in one respect many of their students were deficient; they had not been taught to realize that the object of the industrial chemist, like that of the alchemist, was to produce gold, and that every factory operation must yield a profit, failing which it must cease. In this respect probably our German colleagues were more advanced than we were. In all things the practical side must receive careful attention. The more practical knowledge the chemist had in any branch of industry, the more likely was his work to be successful.

AMERICAN GAS INSTITUTE.

Annual meeting, October 18, 19, 20, 21, 1911, St. Louis, Mo. Officers: *President*, Donald McDonald,

Louisville, Ky.; *Secretary*, A. B. Beadle, 29 West 39th St., New York City.

NATIONAL COMMERCIAL GAS ASSOCIATION.

Annual meeting, October 23-28, 1911, Denver. Officers: *President*, C. N. Stannard, Denver; *Secretary*, Louis Stotz, 29 West 39th St., New York City.

MICHIGAN GAS ASSOCIATION.

September 20-22nd. Annual meeting at Detroit, Mich. *Secretary*, Glenn R. Chamberlain, Grand Rapids Gas Light Co., Grand Rapids, Mich.

AMERICAN INSTITUTE OF MINING ENGINEERS.

October 10th. Annual convention at San Francisco, Cal., followed by trip to Japan. *Secretary*, Joseph Struthers, 29 West 39th St., New York City.

AMERICAN MINING CONGRESS.

September 26-29th. Annual session at Chicago, Ill. *Secretary*, J. F. Callbreath, Denver, Colo.

EDUCATIONAL

ANN ARBOR TO CONFER NEW DEGREE.

The degree of Doctor of Public Health was established by the Board of Regents of the University of Michigan. This degree has long been given in England, and it has recently been given by the University of Pennsylvania. At a conference held a short time ago in Chicago, it was agreed, providing the governing bodies consent, that Pennsylvania, Harvard and Michigan, with the beginning of the next college year, offer practically the same courses.

It has been announced that the Board of Trustees of Cumberland University has elected Prof. J. I. D. Hinds to the chair of Chemistry in that institution. Prof. Hinds has for eight or nine years held the chair of Chemistry at Peabody College. It is stated that he will assume the duties of the new position at the opening of the next fall term.

Dr. E. C. Franklin, prof. of organic chemistry, at Stanford University since 1903, has been appointed professor of chemistry in the Hygienic Laboratory of the U. S. Marine Hospital Service.

Prof. H. V. Army, dean of the Cleveland School of Pharmacy of Western Reserve University, has been selected as the successor of Prof. Virgil Coblentz at the N. Y. College of Pharmacy.

Prof. L. H. Bailey, director of the New York State College of Agriculture of Cornell University, has tendered his resignation to the trustees of the University. It is Prof. Bailey's intention to give up teaching.

At the annual meeting of the British Medical Association, the latter part of July, the University of Man-

chester conferred the degree of LL.D. upon Dr. Russell H. Chittenden, professor of physiology at Yale University.

Dr. Emil Godlewski, professor of agricultural chemistry of the University of Krakau, Poland, has been elected a corresponding member of the Paris Academy of Sciences.

Dr. Stewart J. Lloyd, heretofore adjunct professor of chemistry and metallurgy at the University of Alabama, has been advanced to a professorship of chemistry.

Mr. T. F. Winmill, of Magdalen College, Oxford, has been awarded the Mackennon Scholarship by the Royal Society for his researches on structural chemistry.

Dr. Benj. F. Lovelace, professor of chemistry at the University of Alabama, has been elected associate professor of chemistry at Johns Hopkins University.

Prof. Paul Friedlaender, of Darmstadt, has been awarded the Baeyer gold plaque and the Duisberg prize by the Verein Deutscher Chemiker.

Mr. R. C. Forster has supplemented his previous gifts to University College, London, by an additional £30,000 for the chemical laboratory fund.

Prof. Svante Arrhenius, of Stockholm, has been elected an honorary member of the Academy of Sciences in Vienna.

Prof. Paul Ehrlich, of Frankfort, has been awarded the Liebig medal by the Verein Deutscher Chemiker.

NOTES AND CORRESPONDENCE.

To the Editor of the Journal of Industrial and Engineering Chemistry:

In a communication which appeared in the June number of *THIS JOURNAL* regarding the invention of celluloid, Mr. Edward Worden states that the question whether the credit of the invention belongs to Spill or to the Hyatts is one of fact and not of individual opinion, and goes on in his usual complete and painstaking manner to cite the references, patents and decisions bearing on the subject.

The writer, in reply, begs leave to make use of Mr. Worden's data, to which the reader is referred, but to draw different conclusions from it.

While it is true that Parkes was the first to take out a patent into which the statement may be read that he knew of the solvent action of a solution of camphor in absolute alcohol, yet it was Daniel Spill who brought out the vital fact that nitrocellulose becomes plastic by admixture with camphor, commercial alcohol merely being used as a vehicle, and it is upon this fact that the subsequent development of the industry rests.

Celluloid was made by the Hyatts some years later by an alleged new process and they should be given full credit for the pioneer work which put the industry on a commercial basis (R. C. Schüpphaus, "The Evolution of Smokeless Powder," *J. Soc. Chem. Ind.*, Vol. XIV, No. 6; R. C. Schüpphaus, "Technical Application of Camphor," *J. Soc. Chem. Ind.*, Vol. XXVI, No. 8). The material is now manufactured under several trade names, but the term celluloid has generally come to be used to designate the various products, and it is in this sense that Spill is credited with having invented celluloid. C. M. JOYCE.

ARLINGTON, N. J.,
June 14, 1911.

To the Editor of the Journal of Industrial and Engineering Chemistry:

I should like to correct a typographical error in a paper of mine in the October, 1910, number of *THIS JOURNAL* on "The Determination of Sugar Lost by Entrainment from Evaporators." In formula II, near the end, the letter I should be a figure 1.

R. S. NORRIS.

HONOLULU, July 31, 1911.

To the Editor of the Journal of Industrial and Engineering Chemistry:

I think attention should be called to the danger of accepting weights for standard solutions and the equivalent values in substances as given in well-known standard works.

The latest edition of Sutton's "Volumetric Analysis" (the 10th ed.) pretends to have carefully revised the text, corrected mistakes and brought values in harmony with the atomic weights to be used in 1911.

Faith in the claim will be rudely broken by a glance at page 395: The quantity of potassium bichromate to be taken to make the standard solution for the

analysis of glycerines is the old figure, familiar for the past 25 years. It was wrong twenty-five years ago, according to tables of atomic weights most in use, and it has remained wrong ever since. It has been reprinted in every book dealing with glycerine analysis and is a good example of how little real revision there is in standard books.

In comparison with the accepted atomic weights of today a glycerine would test about 0.3 per cent. too low on a basis of 100 per cent. glycerine by using 74.86 grams (the figure in Sutton) instead of the accepted figure of today, 74.5641 grams.

The analysis of crude glycerines is difficult enough, and full of enough pitfalls, without having to start on a wrong basis.

The glycerine industry is a large and very important one, and such inaccuracies as reprinted in Sutton should be shown up strongly, both as a guide to the users of the book and as a warning to the publishers. The amount of trouble that can be caused by the use of these incorrect figures is something little appreciated, for while a spread between analysts of 0.3 per cent. might be passed, or even 0.5 per cent., when 0.3 per cent. more is added on trouble is at hand.

WILSON H. LOW.

LABORATORY OF
THE CUDAHY PACKING CO

A FEW LABORATORY HELPS.

Sometimes insignificant things which are developed in any particular laboratory are never taken advantage of by other people for the very reason that they are considered by the originator as so trivial that they are not worth publishing and so do not become known.

It has occurred to me that a few devices which we are constantly using might be of interest to others.

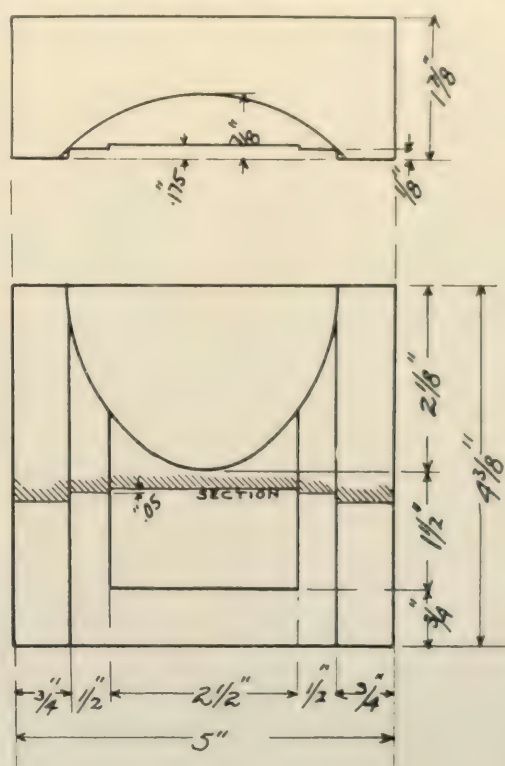
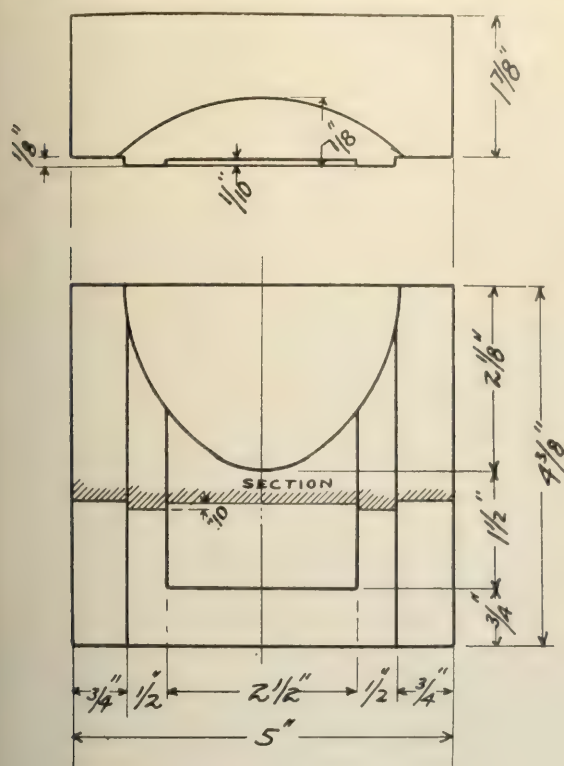
Test Samples.—It is a frequent occurrence in the case of open-hearth alloy steels that the ladle test as usually taken from a heat are too hard to drill even with the aid of the most modern high-speed steel drills; and sometimes if the carbon content happens to be at all unusual, a good deal of difficulty is experienced in annealing the test to get it into condition to drill. This is particularly undesirable in the case of a rapid test for the melter during the progress of a heat where the delay of even a few minutes might be very costly. This may seem an absurd statement to men who are accustomed to make carbon steels and who judge largely by the fracture, but the conditions are often far different when alloy metals are present, and it often happens that the melters would be at a very considerable disadvantage in securing a uniform product without the assistance of the laboratory in keeping them informed of the changing composition of the metal during the melting.

In order to overcome any possible delay in getting our samples we designed a split mould (see sketch) in which is cast a thin sheet of metal. A ladle sample is drawn from the furnace and poured directly into

the mould, which is knocked apart immediately and the small casting quenched in water. The heavy end of it is then broken off and the thin piece sent to the laboratory where it is crushed to a fine powder in a steel mortar similar to the one described in *Blair*, p. 17, 7th ed. The behavior of the piece during the crushing is a very fair indication of the percentage of carbon. When the metal has reached 0.30 per cent. carbon the brittleness begins to give way to malleableness, and this latter property increases as the carbon decreases beyond this point. The direct

in gasoline keep in excellent condition. The thin coat of paraffine is not enough to be objectionable and yet it is thick enough to cause water or acid spilled upon it to form into a well rounded drop which can be easily brushed off. In fact, if the bench is made to slope a little, the water or acid will run off almost of its own accord.

Gas.—If the location of the laboratory is such that there is no chance to connect with the usual city gas pipes, gasoline gas is the customary substitute. So it was with us, but we have found that by making



DETAIL OF TEST MOULD

combustion method should be used for carbon determination (*THIS JOURNAL*, I, 376.).

The moulds are also used in taking the final samples during the casting of the ingots in the pit. The method is not only very rapid but it is also very accurate and the sample obtained is always of uniform analysis.

Boats for Carbon Combustion.—We have had considerable success in using boats made of nickel. It is very easy to make them up and they last quite a long time. Ground quartz is used as a bed for the drillings. In buying nickel sheets for such purpose some care must be used in the selection in order to get nickel free from carbon. We generally use sheets of 0.03 inch thickness.

Benches.—The problem of a bench that will stand the wear of a busy laboratory is not always an easy one. Slate and glass are of course very nice, but they are probably responsible for a good deal of breakage of glassware. We have found that wooden benches painted occasionally with a solution of paraffine

a very slight change in the generator—one which any pipe fitter can readily accomplish—that ordinary producer gas can be substituted for the air supply and mixed with the gasoline gas in such proportions as to enrich it into a very efficient gas. We find the most economical mixture to be 80 per cent. producer gas plus 20 per cent. gasoline gas.

Producer gas is not always available for such a purpose, but in plants where it is employed, its use in this way will not only result in a greater satisfaction but also in a reduction of the gasoline consumption. It should be passed through a scrubber or some equivalent device to remove tarry matter before being piped to the gasoline mixer. No storage tank is necessary other than the mixing chamber which comes with the usual gasoline gas outfit. The only precaution to observe is the insertion of wire gauze at some point in the pipe line to prevent back fire.

Hood Linings.—It is sometimes desirable to build an inexpensive but efficient hood in the laboratory. Such materials as tiling, soapstone or glass are very

much to be preferred, but if a good serviceable structure is desired at small cost a wooden one lined with "Century" asbestos shingles is excellent. These shingles make a nice appearance and are supposed to be acid-proof. Strictly speaking, they do not effectually resist acid under the severe conditions, but when coated with pitch they are very efficient. There is also the further advantage that when thus coated the acid fumes do not condense on the surface and drop down on the work—a thing which frequently occurs in most hoods, especially in humid weather.

If any readers are interested in further details of the above devices I shall be glad to answer any questions they care to address me.

WM. H. KEEN, CHEMIST,
FIRTH-STERLING STEEL COMPANY,
WASHINGTON, D. C.

GROWTH OF A NEW INDUSTRY.

BY-PRODUCTS IN COKE-MAKING COMING TO BE RECOGNIZED AS WORTH SAVING. HUNDREDS OF MILLIONS OF DOLLARS' WORTH OF GAS, TAR, AND AMMONIA WASTED. INCREASE IN COKE PRODUCTION.

For many years the valuable material constituting the by-products in the manufacture of coke was absolutely wasted; even to-day there is great extravagance in coke-making, through the continued use by the majority of manufacturers of the old beehive type of coke oven, rather than the by-product oven. The United States is far behind Germany and other foreign countries in adopting the economies resulting from the coking of coal in by-product ovens. In what is known as the beehive oven, so called because of its similarity in shape to the conventional beehive, the coal is only partly consumed, or, to speak more properly, the volatile, combustible constituents, the gas, tar, and ammonia—everything except the fixed carbon, which is left behind as coke—is wasted. In the by-product ovens these are recovered and used. In Germany little or no coke is now made except in retort or by-product ovens. Hundreds of millions of dollars' worth of these valuable by-products have been wasted by American coke producers, but it is gratifying to note that the improved by-product oven is replacing the wasteful beehive with considerable rapidity.

The first ovens of the by-product type in the United States were built in 1893 at Syracuse, N. Y. From this one plant there has been an increase to 4,078 by-product ovens in 1910, all but 27 of which were in active operation. This is an increase of 164 over the number in operation in 1909 and 399 more than were in operation in 1908.

CONSERVATION OF THE BY-PRODUCTS.

During 1909 and 1910, according to E. W. Parker, of the U. S. Geological Survey, there was more activity in the construction of by-product recovery coking plants than at any time since 1903. At the close of 1909 there were 649 by-product ovens in course of construction, with 300 more contracted for. Of the 649 ovens started in 1909, there were 99 completed and put in blast in 1910. Work on the 300 ovens contracted for in 1909 was begun in 1910

The production of coke in by-product ovens in 1910 amounted to 7,138,734 short tons, against 6,254,641 tons in 1909 and 4,201,226 tons in 1908. The increase in 1910 over 1909 was 14.13 per cent., whereas the total production of beehive coke increased from 33,060,421 short tons to 34,570,076, a gain of 1,509,655 tons, or only 4.57 per cent. The coke made in by-product ovens in 1910 was 17.12 per cent. of the total production.

ECONOMIES IN THE BY-PRODUCT OVENS.

The efficiency of by-product ovens is shown by the fact that while the beehive ovens in 1910 produced 34,570,076 short tons of coke on a consumption of 53,559,285 short tons of coal, or 64.54 per cent., the retort ovens in the same year produced 7,138,734 short tons of coke on a consumption of 9,529,042 short tons of coal, or 74.9 per cent.

The figures compiled by the Geological Survey show that the average cost of the coal consumed in the by-product ovens in 1910 was \$2.18 a ton, against \$1.10 a ton for that used in the beehive ovens, but the difference in these values is due to the fact that the beehive practice the transportation charges are borne by the coke, and as retort oven plants are located at a distance from the mines, the freight item is charged to the value of the coal used in them. If, however, the expense of transportation on beehive coke from the ovens to the points of consumption is added to the value of the coke it will probably be found that the cost of the beehive coke at the furnace has exceeded that of the by-product oven coke.

WEALTH IN THE BY-PRODUCTS.

The total value of the by-products obtained from the manufacture of coke in retort ovens in 1910 was \$8,479,557, or a little more than one-third of the value of the coke produced—\$24,793,016. In 1909 the value of the by-products amounted to \$8,073,914, and in 1908 to \$7,382,299. The by-products recovered in 1910 consisted of 27,692,858 cubic feet of surplus gas, valued at \$3,017,908; 66,303,214 gallons of tar, valued at \$1,599,453; 70,247,543 pounds of ammonium sulphate, or its equivalent, valued at \$1,841,011; 20,229,421 pounds of anhydrous ammonia, valued at \$1,725,266; and 4,654,282 gallons of ammonia liquor, valued at \$295,868. In addition to these, there is a quantity of light and secondary oil and small quantities of coke breeze recovered, with an estimated value of \$400,000. The value of the recoverable but wasted contents of the coal made into coke in beehive ovens would, at the prices obtained in 1910, have been between \$35,000,000 and \$40,000,000.

If all the coke made in the United States were produced in retort ovens, says Mr. Parker, probably not more than half the number of ovens would be required, say, for 1910, 45,000 ovens. These would yield in gas, over and above that required for the regeneration of the ovens, without by-product recovery, approximately a million horsepower per hour or every day in the year.

CONSULAR AND TRADE NOTES.

MARSEILLAISE PEANUT-OIL INDUSTRY.

The arrivals of peanuts at Marseilles during the calendar year 1910 aggregated 348,016 metric tons, classified as follows: Decorticated, or shelled, nuts, 199,774; undecorticated, or unshelled, nuts, 148,242 tons. Taking into account the weight of the hulls, it may be said that the receipts of decorticated peanuts were practically twice as large as those of peanuts in the shell.

A detailed statement of these imports showing the relative importance and range of values of the different varieties of peanuts sold in the Marseillaise market during 1910 follows, the quantities being given in metric tons of 2,204 pounds:

Articles and countries.	Quantity Tons.	Range of values per 220 pounds.
<i>Decorticated.</i>		
China.....	24,071	\$6.65 to \$8.21
Mozambique.....	9,485	7.14 to 8.49
Bombay.....	14,821	6.51 to 7.81
Coromandel Coast.....	151,397	5.86 to 7.52
Total.....	199,774	
<i>Undecorticated.</i>		
Rufisque and Sine.....	90,676	\$5.40 to \$6.85
Gambia and Saloum.....	38,696	5.40 to 6.65
Casamance.....	820	5.26 to 6.30
Bissao.....	2,455	6.22 to 6.32
Rio Nunez.....	204
Egypt, India, and Java.....	15,297	5.49 to 6.27
Spain and La Plata.....	94
Total.....	148,242	

USE OF DIFFERENT VARIETIES—PRICES OF OIL.

It will be observed that the unshelled nuts bring relatively higher prices than those which arrive here already shelled. In fact, edible oil is made principally from the West African nuts, the best grades being obtained from the following varieties, in the order named: (1) Senegal nuts: (a) Rufisque Cayor, (b) Nianing, (c) Sine, (d) Saloum; (2) Gambia; (3) Casamance; (4) Rio Nunez (French Guinea). The shelled peanuts enter mostly into the manufacture of industrial oils, although the Mozambique and selected Bombay nuts furnish current grades of edible oil. The Java peanuts are taken up largely by the confectionery trade, important quantities having been re-exported to the United States during the last two years.

Peanut oil ranks next to olive oil in popular favor, being generally preferred in France to cotton oil. It is highly rated as a salad and cooking oil, and is used extensively in the manufacture of margarin and by sardine packers. It is frequently mixed with olive and other vegetable oils. The industrial grades obtained from the Indian nuts and the second pressings of the African varieties are consumed mainly by the soap-making industry, but a certain proportion is also employed for illuminating and lubricating purposes.

The price of peanut oil varies considerably from year to year. The average Marseillaise values, during the last three years, of edible oil made from Gambia nuts, which furnish a good medium quality, were as follows per 100 kilos (220 pounds): In 1907-8, \$18.56; 1908-9, \$14.67; 1909-10, \$16.98. The oil extracted from the Rufisque peanuts is usually worth from 5 to 10 per cent. more than the Gambia oil. The following are the ruling prices at the present time (May 17) per 100 kilos f. o. b. Marseilles, naked: Edible grades—Rufisque selected, \$19.30; Rufisque superfine, \$18.14; Rufisque petite, \$16.40; Gambia, \$17.37; Mozambique, \$16.40; Bombay, \$16.21. Industrial grades—lamp oil, \$15.05; lubricating oil, neutral, \$14.86; soap oil, \$12.64.

PRODUCTION AND PRICE OF PEANUT OIL.

The Marseillaise mills produced 1,141,000 (1,100,000 metric) tons of oil cake, the value ranging from 12 to 10 francs (\$2.70 to \$2.25) per 100 kilos delivered in bulk, ex-mill. The cake is used for cattle-feeding. About 80,000 tons are exported annually, chiefly to Germany and Scandinavia. The present ruling prices of the various grades of peanut cake and competing products in this market are as follows:

Articles	Price
<i>Peanut:</i>	
Rufisque	
Extra white.....	\$3.00
Ordinary.....	2.70
Coromandel.....	2.60
<i>Sesame</i>	
Karachi.....	2.60
Indian.....	2.31
Cotton, first quality.....	2.70
Cornmeal.....	4.24
Linseed.....	4.44
<i>Copra:</i>	
Ordinary.....	2.60
Semiwhite.....	2.84
Ceylon.....	2.79
Cochin.....	4.05
Colza, Russian.....	1.93

CLEANING AND PRESSING OF NUTS.

Peanuts in the shell are never ground whole in the Marseillaise mills. On the contrary, expression of the oil is almost invariably preceded by a careful preparation of the nuts, particularly in the case of edible oil. The peanuts are crushed only after having been cleaned and decorticated, and after every effort has been made to remove entirely the germs and the red skin covering the kernels. All these operations are done by machinery.

The peanuts undergo a preliminary cleaning in a "blutoir," or rotary sieve; they are afterwards brought by an elevator to the decorticating machine and passed through grooved rollers, so adjusted as to husk the nuts without crushing the kernels. The separation of the husks and kernels is effected by ventilation. The germs, sprouts, and red skin still adhering to the kernels after the husking process are stripped off by friction against the coarse-wired meshes of a rapidly oscillating sieve, the operation being completed by a ventilator connected with the apparatus. It is extremely difficult, however, to detach entirely the red cuticle from the kernels, and in the case of new-crop nuts it is said to be a practical impossibility.

After the kernels have been cleaned they are ground by a crusher provided with two pairs of rollers. The mass emerging from the rollers falls into a "sasseur," or sifter, which separates the coarse from the fine meal, the remaining stones and other foreign substances having been eliminated by an aspirator. The coarse meal is reground.

PRESSING OF THE MEAL.

The meal is then put into hair bags called "scourtins," and subjected to hydraulic pressure, from 12 to 15 scoutins separated by metal plates being pressed at the same time. A scoutin contains about 10 kilos (22 pounds) of meal. The type of press employed in connection with this method is known as the "presse Marseillaise." Most of the presses of this type are worked under a pressure of 250 atmospheres, or 3,675 pounds to the square inch, but a pressure of 500 atmospheres is not infrequent. A few of the leading Marseillaise mills have adopted the Anglo-American "cage press," thus avoiding the use of scoutins. While the Marseillaise press crushes only from 1,000

to 1,100 kilos of nuts per day of 24 hours, the capacity of the Anglo-American cage press reaches 2,000 to 2,500 kilos.

The first pressing, which furnishes the high-grade oil, is made without heating the meal. In other words, the meal is pressed cold. This pressing usually lasts about one hour. For the second pressing the scourtins are generally emptied, the meal reground and brought to a temperature of 30° to 50° C. (86° to 122° F.), according to the quality and condition of the nuts. The same amount of pressure is applied as for the first pressing and the same press may be used. A smaller yield but a finer grade of oil results from the second pressing when the supplementary grinding of the meal is dispensed with. In some mills a third pressure is applied, but this is an unusual practice.

YIELD OF OIL.

The yield of oil varies according to the origin and condition of the nuts. The Senegal peanuts in the shell yield about 33 per cent. of their gross weight, the Gambia peanuts 31.5 to 32 per cent. Both of these varieties yield from 21 to 23 per cent. on the first pressing and 10 to 11 per cent. on the second pressing. The average oil yield of the shelled peanuts is about 39 per cent. for the Indian nuts and 42 per cent. for the Mozambique. From 6 to 10 per cent. of oil, with an average of 8 per cent., remains in the cake. A bushel of shelled peanuts weighing 30 pounds should produce on the average about 1 $\frac{1}{3}$ gallons of oil (a little over a gallon on the first pressing) and 16 $\frac{1}{2}$ pounds of cake, hulls not included. These cakes are about 2 feet square by $\frac{3}{4}$ inch thick.

After running from the presses, peanut oil does not need refining, but is simply filtered. It is then fit for consumption as salad oil. Bleaching is resorted to only in order to produce the white oil required in the manufacture of margarin.

Extraction of oil by solvents has not been found profitable in the case of peanut cakes, as these cakes are used exclusively, except when in a damaged condition, as a stock feed, and such solvents as sulphide of carbon and tetrachloride of carbon are considered harmful and depreciate the value of the cake for cattle-feeding purposes. Only a very limited quantity of peanut cake is ground into meal, and this always on special demand.

USE OF HULLS—ANALYSIS OF CAKE.

The hulls are rarely, if ever, mixed with the cake, but they are largely used as fuel by the mill owners. They are also ground separately and disposed of as a by-product of small value. After grinding to meal they are worth from 3 to 3.50 francs (58 to 67 cents) per 100 kilos, packed in bags. Considerable quantities of this meal are shipped to England, where, it is stated, it is mixed with molasses in the manufacture of a compound cake which has lately come into favor as a stock feed. It is stated that the hulls are used to a certain extent in Germany as paper stock.

The following is an official analysis of West African peanut cakes: Moisture, 9.72 per cent.; oil, 5.68 per cent.; feculae and digestible carbohydrates, 36.08 per cent.; protein, 40.05 per cent.; nitrogenous substances other than protein, 1.07 per cent.; crude fiber (not digestible), 3.86 per cent.; mineral substances, 3.54 per cent.

As shown by this analysis, the peanut cake contains an extremely large percentage of nitrogen, which accounts for the fact that use of the meal in army and navy rations and by the working classes has been occasionally advocated.

ADAPTATION OF COTTON-OIL MILLS TO PEANUT CRUSHING

The adaptation of cotton-oil mills to the peanut-oil industry can be accomplished at a moderate expense. The following estimate of the cost of the special equipment required in order to treat 50 metric tons of peanuts per day of 24 hours has been furnished by a Marseillaise firm that makes a specialty of this type of machinery:

	Cost.
One "blutoir," or bolter, total length 4 meters (13.12 feet), complete.....	\$550.05
One decortivating machine, with 3 grooved rollers, and a ventilator to remove the stones and other foreign substances still adhering to the shells; a sieve for the separation of the hulls and kernels; another ventilator for the removal of the shells having passed with the kernels through the sieve, and pulleys.....	868.50
One ventilator, with distributor, for the collection of the undecorticated peanuts having passed with the hulls.....	125.45
One sorting apparatus for the kernels remaining in the waste drawn off by the ventilator of the decortivating machine.....	250.90
One apparatus receiving the kernels from the foregoing and removing the stones and red skins, and separating besides the germs and coarse bran.....	250.90
One elevator to bring the nuts from the "blutoir" to the decortivating machine, 7 meters (22.96 feet) in height.....	140.89
One elevator, to feed the apparatus handling the clean kernels.....	110.97
One elevator to feed the apparatus handling the waste.....	110.98
One endless screw to carry waste from the decortivating machine.....	77.20
One endless screw to carry the clean nuts from the "blutoir" to the decortivating machine.....	77.20
One aspirator for the entire installation.....	144.75
Driving gear for the entire installation.....	231.60
Total cost, delivered quay Marseilles.....	2,939.39

The same installation with wooden frames and supports would cost \$2,316.

A crushing machine complete, with a capacity of 50 metric tons, could be had for \$874.29, divided as follows:

	Cost.
One hopper, with distributor, above crusher....	\$ 67.55
One crusher, comprising 2 pairs of rollers, the first pair measuring 400 millimeters (1.31 feet) in diameter, and 600 millimeters (1.968 feet) in length, and the second pair 600 millimeters both in length and in diameter.....	482.50
One "sasseur," or sifter, placed beneath the crusher, removing the foreign substances and classifying the meal.....	115.80
One aspirator connected with the rollers and the "sasseur".....	208.44

The presses and filters employed in cotton-oil mills are suitable for the peanut-oil industry.

THE RADIUM MARKET.

[From Consul General T. St. John Gaffney, Dresden, Germany.]

Since the discovery of radium and the powerful action of its rays, governments as well as numerous private enterprises have endeavored to discover or acquire suitable sources of this valuable product. While governments are prompted exclusively by scientific motives, private individuals to a very great extent are attracted by the high price, \$80,000 per gram (0.03527 avoirdupois ounce). The cost of producing a gram of radium is about \$2,000, which is low considering the value of the substance.

A radium bank was established in Paris a short time ago, which in 1910 disposed of 1.92 grams of radium of highest activity at \$80,000 per gram. Of that quantity \$15,000 worth has been acquired for industrial purposes and \$139,000 worth for use in therapeutics.

Radium of the highest activity never loses any of its properties. A regular output of radium means a regular increase in the quantity of radium in existence in the world. In consequence of this property, a hiring system has been developed, a procedure which will naturally hamper the development of a market.

The production of radium is dependent to a great extent upon the production of uranium, and as the present output of the latter metal is still needed to meet the demand for uranium-color manufacture, an early increase in the production of radium seems unlikely. The new American production of inferior uranium has also interfered with the market, and a regular increase in the output will cause still further depression.

Radium is found in Luntwengule, Morogoro district, East Africa; Evje N. v. Cristiansund, Norway; Cornwall and South Devon; Joachimsthal in Bohemia; Gilpin County in Colorado; and Kolmlagerstaetten in Sweden. Of all uranium mines only the one at Joachimsthal, which is working regularly, may be depended upon; there the two mines to be taken into account which have an estimated yearly output of 16 to 20 tons of uranium pitch ore, or pitchblende, containing 55 per cent. U_3O_8 . Radium-free uranium color is obtained from this ore, which increases the radium content of the residue. Six tons is the annual production of residue, from which it is reasonable to expect a production of 1.8 grams of radium salt of the highest activity.

The yield in Austria up to the present—3.5 grams—is not derived from the regular production from pitchblende, but from numerous old stocks, which are probably exhausted now. The yearly yield of 1.8 grams of radium salt of the highest activity may, according to present prices, be valued at \$144,000.

[Previous reports on radium appeared in Weekly Consular and Trade Reports for Apr. 16, 1910, and in Daily Consular and Trade Reports for July 21, Aug. 30, Sept. 27, and Nov. 23, 1910.]

PEACE IN THE GERMAN POTASH INDUSTRY.

[From Consul Talbot J. Albert, Brunswick.]

At the conference held recently at Hamburg between the conflicting interests, German and American, in the potassium industry, an agreement has been reached as to prices and rebates.

The agreement has a duration of five and one-half years. During this period the American purchasers of potash, that is to say, the North Trust, the South Trust, and the independents, obligate themselves to make all purchases from the potassium syndicate. The probability of the market being disturbed by outside mines is thought to be remote, as such outsiders would have to organize a sales agency in the United States similar to the German Kali Works owned by the syndicate, which delivers potash salts directly to the buyer. Such an organization would be expensive and difficult to effect.

The basis of prices is practically the same for concentrated salts as that contained in the potassium law, and the same as prevailed in America in 1909 before the syndicate was renewed and before the Schmidtmann contracts went into force. The prices, aside from 40 per cent. manure salts, which are sold to the German agriculturists at low prices, are the same as the maximum prices laid down in the law for the domestic consumption. On the other hand, the prices proposed for raw salts, especially for kainit, are higher than the prices formerly paid by Americans to the syndicate. Rebates for most sorts of salts are increased. Formerly a rebate of 9 per cent. on the average was granted the American companies. Now it will be from 11 to 12 per cent.

In reference to certain expenses which may be incurred by the syndicate the right is granted it during the duration of the agreement, five and one-half years, to increase prices 3 per cent.

The agreement is incomplete inasmuch as the Aschersleben and Sollstedt Works belonging to the Schmidtmann interests and the Schmidtmann International Trust had not united in it. An effort will be made by amicable means to bring the remaining parties into the agreement. If it is not successful, it is thought that their sales contract will be attacked, as they are regarded as in some respects legally indefensible.

EIGHTH INTERNATIONAL COTTON CONGRESS.

[By Correspondent ALBERT TALBOT, M. C. C. B.]

The International Cotton Congress which was held in Barcelona, Spain, May 8 to 11, 1911, was a representative gathering of cotton manufacturers from all parts of the world. More than 250 delegates were present, representing every country in which the cotton industry is carried on, with the exception of Japan and Russia.

Papers were read and discussed which related to the subject of cotton manufacturing in all its stages and the problems confronting the industry to-day. Among these subjects may be mentioned the expansion of the present cotton fields and the opening up of new ones in any part of the world where this can be done with success to meet ever-increasing requirements; the more scientific cultivation of the raw material; improvements in the ginning, baling, warehousing, and transporting of cotton, especially American cotton, by which large savings can be effected; the international standardization of grades of cotton, and reforms in the marketing of same; plans for the application of world-wide short-time running, to deal with the over-production of cotton goods and the consequent universal depression in the industry and trade; mill-fire insurance problems; the drafting of a uniform contract for the purchase and sale of yarns and cloth; and the establishment of a table of percentages of moisture to apply to cotton yarns.

THORIUM SYNDICATE SUSPENDED.

[Special Correspondence in London Financial Times.]

For a considerable time past negotiations have been proceeding among the principal European manufacturers of thorium with the view of coming to an arrangement by which production and prices could be regulated, but these have at length been abandoned, as unanimity was found to be unattainable under existing circumstances. The supply of thorium was at one time a virtual monopoly under the control of a powerful Continental syndicate, but the "corner" has at length been broken, and the industry has fallen on evil days from the producer's point of view. Prices have steadily declined for two or three years, and are not unlikely to go considerably lower. This declining tendency is directly attributable to the glutting of the market with monazite sand, the principal raw material from which thorium is produced. The supplies of this sand were entirely controlled by the syndicate, whose exorbitant prices forced the leading makers of incandescent mantles, including the incandescent-light companies, to exert themselves to obtain independent supplies at all costs. In this they were successful and prices fell rapidly. Practically the whole of the supply of monazite sands comes from Brazil, and thorium nitrate is manufactured only in the United States and on the continent of Europe. The yearly consumption of monazite sand for the manufacture of thorium is placed at between 2,000 and 2,500 tons, but for some years the supplies have been equal to double the consumption. The contract between the Brazilian Government and the thorium syndicate has now expired, and a new lease of the fields is about to be arranged. There are numerous offerers, and as the Brazilian Government is not likely to allow any monopoly to acquire control of the supplies a further flooding of the market and consequent decline in prices is feared.

NEW EDITION OF GERMAN TARIFF.

A revised edition of the tariff of the German Customs Union has been published in English by the Bureau of Manufactures (Tariff Series No. 7). This edition includes all corrections up to June, 1911. In view of the fact that the changes, except those embodied in Supplement A to the former edition, and those noted from time to time in the Daily Consular and Trade Reports, are of minor importance. Copies of the new edition will not be sent to persons on the mailing list for tariffs, but may be obtained from the Bureau of Manufactures upon application.

NEW RADIUM SPRING IN BOHEMIA.

[From Consul William J. Pike, Reichenberg, Austria.]

In the neighborhood of Reichenberg a radium spring has been discovered whose waters are remarkably strong in radioactivity. The measurement of experts by the newest apparatus shows an emanation quantity of 18.8 Mache units, which is double the amount of the celebrated Bohemian spring at Teplitz. For medicinal purposes the waters are said to be most satisfactory,

having a temperature of 7.7°C ., and a constant flow of sufficient quantity for an important establishment. — *Daily Commercial and Trade Reports*, Aug. 7.

In the second quarter of 1911 the American consulate at Cologne, Germany, invoiced \$500,323 worth of aniline so and dyes to the United States, also \$190,044 of mineral water and other articles, making up a total of \$1,180,231.

BOOK REVIEWS.

Handboek ten Dienste van de Suikerriet-Cultuur en de Riet-suiker-Fabricage op Java. Edited by the United Sugar Experiment Stations of Java. 4 volumes. Amsterdam: J. H. de Bussy.

The first three volumes of the "Handboek" were reviewed in *THIS JOURNAL*, 1, 380. Those who have read the recent interesting contributions upon the sugar cane industry in different countries written by Mr. H. C. Prinsen Geerligs in *De Indische Mercur* will be glad to know that this entire series of articles with much added information has been incorporated in permanent book form to make a new volume of the "Handboek." Vol. IV, "De Rietsuikerindustrie in de Verscheidene Landen van Productie." Historisch technisch en statistisch overzicht over de productie en den uitvoer van de reitsuiker. By H. C. PRINSEN GEERLIGS, Directeur der Filiale Nederland van het Proefstation voor de Java Suiker Industrie. 1911. 416 pages. Price, bound, f. 7.50.

In the introduction to this new work Mr. Geerligs states that owing to several causes—(chief among which he gives the Brussels Sugar Convention of 1902, the Annexation of Formosa by Japan, and the changed conditions resulting from the Spanish-American War)—the cane sugar industry has entered upon a new period of development. He considers the present moment, therefore, an opportune one in which to review the conditions and future prospects of the industry.

In the first 42 pages of the volume a brief survey of the entire field is given in which connection the author reviews the history of the sugar cane industry from the first legendary mention of the cane in the sacred writings of the Hindoos down to the present day. Special stress is placed upon the influences of such movements as the Crusades, Spanish Colonization, Negro Slavery, The Continental Blockage, The Rise of the Sugar Beet Industry, The Bounty and Cartel System, and the Recent Brussels Convention.

In the second and main division of the work the

conditions of the cane industry in each of some countries are described. The geography and climate of each section, agricultural conditions, methods of cultivation and manufacture, character of labor, conditions of marketing the raw sugar, and statistics of production are thoroughly reviewed. Colored maps of the leading cane-producing countries, photographs of modern factories, and numerous cuts and diagrams give additional value to the descriptive matter of the text.

The typography of the book is excellent, conforming in character to the work of the publishers upon the three previous volumes of the "Handboek."

The many friends of Mr. Geerligs in all parts of the sugar world are pleased to note that his retirement from active labors in Java, in building up the sugar industry of that colony, has brought with it, not a cessation of activities, but the opportunity of rendering even greater services in other ways.

It is hoped that this new addition to the "Handboek" may soon be translated into English for the benefit of those readers, who are unable to find their way in Dutch.

C. A. BROWNE

"Royaume de Belgique Ministres des Colonies, Bulletin Agricole du Congo Belge." Brussels. December, 1910. Vol. I, no. 2. Price, 5 francs a year.

This is the quarterly agricultural journal of the Office of the Minister for the Colonies. Its contents are almost entirely of an agricultural nature, giving the rules and regulations for setting out of rubber plantations, a review taken from *Technique Moderne* on rubber latex, discussing in detail the various methods of coagulation, the working of raw rubber, the composition of the latex, its valuation and selling methods. An article on dry farming deals principally with the practice in the Western United States, and several articles discuss introduction of live stock into the Belgian Congo. A botanical description (in Dutch) is given of the various commercial rubber trees. The journal is well printed on good paper and is full of illustrations.

R. F. BACON

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

Materials for Permanent Painting. By MAXIMILIAN TOCH. D. Van Nostrand Company. 208 pp. \$2.00 net.

Chemistry of the Essential Oils and Artificial Perfumery. By ERNEST J. PARRY. 2nd Ed. D 8vo. 550 pp. \$3.50. London: Scott, Greenwood & Son.

Manual of Agricultural Chemistry. By HERBERT INGLES. 2nd Ed. D 8vo. 450 pp. \$2.25. Scott Greenwood & Son.

Directory of Chemical Industries throughout the World. 1st Ed. 1911. L 8vo. 727 pp. \$3.75. Berlin. 1911.

Translocation of Plant Food and Elaboration of Plant Material.

- in Wheat Seedlings. By J. A. LE CLERC AND J. F. BREAZEALE. U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin 138.
- The Dimethyl Sulfate Test of Creosote Oils and Creosote Dips. A Substitute for the Sulfonation Test. By ROBERT M. CHAPIN. U. S. Dept. of Agriculture, Bureau of Animal Industry, Circular 167.
- Application of Physico-chemical Theories to Technical Processes and Methods of Manufacture. By R. KREMANN. \$2.50. Halle. 1911. (German.)
- Detection and Determination of Small Quantities of Ethyl and Methyl Alcohol and of Formic Acid. By RAYMOND F. BACON. U. S. Dept. of Agriculture, Bureau of Chemistry, Circular 74.
- Handbook on the Manufacture of Illuminating Gas. By WILHELM BERTELSMANN. 2 vols. Vol. I. 581 pp. \$5.00. Stuttgart: Ferdinand Enke. (German.)
- Handbook of Chemical Technology. By H. OST. 7th Ed. \$4.00. Hannover: Max Jaenecke. (German.)
- Mixing, Stirring and Kneading and the Machines Used for these Operations. By HERMANN FISCHER. 8vo. 90 pp. \$1.75. Leipzig: Otto Spamer. (German.)
- Theory and Practice of the Gas Industry. By RUDOLF MEWES. 40. 403 pp. \$5.00. Leipzig: H. A. L. Degener. (German.)
- The Patent Laws of All Countries. By J. KOHLER AND M. MINTZ. Vol. II, Part 5. L. 8vo. \$4.25. Berlin. 1911. (German.)
- The Mineral Industry. Vol. XIX. By ALBERT H. FAY. 8vo. 900 pp. \$10.00. New York: McGraw, Hill Book Co.
- Catalysis. By WILHELM OSTWALD. 2nd Ed. 8vo. 39 pp. \$0.50. Leipzig: Akademische Verlagsgesellschaft. (German.)
- Saccharin in Food. U. S. Dept. of Agriculture, Food Inspection Decision No. 138.
- Notices of Judgment, Food and Drugs Act, Nos. 895 to 987. U. S. Dept. of Agriculture.
- Crystallography and Practical Crystal Measurement. By A. E. H. TUTTON. 8vo. 946 pp. \$8.50. The Macmillan Co., New York.
- Rubber. By P. SCHIDROWITZ. 8vo. 290 pp. \$2.75. Methuen & Co., London.
- Metallurgy. By W. BORCHERS. Translation. 8vo. 271 pp. \$3.00. John Wiley & Sons, New York.
- Laboratory Manual of Inorganic Chemistry. By E. C. BINGHAM AND GEO. F. WHITE. 12mo. 147 pp. \$1.00. John Wiley & Sons, New York.
- Technical Methods of Ore Analysis. By ALBERT H. LOW. 5th Ed. John Wiley & Sons, New York.
- Manual of Practical Assaying. By H. V. F. FURMAN AND WM. D. PARDOE. 7th Ed. 8vo. 530 pp. \$3.00. John Wiley & Sons, New York.
- Essentials of Volumetric Analysis. By HENRY W. SCHIMPF. 2nd Ed. 12mo. 358 pp. \$1.50. John Wiley & Sons, New York.
- Short Introduction to the Structure of Iron-Carbon Alloys. By O. KROHNKE. \$1.75. Berlin. 1911. (German.)
- Chemistry of the Albuminoids. By COHNHEIM. 3rd Ed. \$2.75. Brunswick. 1911. (German.)
- Biochemical Metabolism of the Phosphate Ion in Soil. By J. STOKLASA. L. 8vo. 159 pp. \$1.50. Jena. 1911. (German.)
- Textbook of Pharmaceutical Chemistry. By TH. EKECRANTZ. 8vo. 288 pp. \$2.75. Stockholm. 1911. (Swedish.)
- The Methods of Testing of the Austrian Pharmacopoeia. By G. MOSSLER. L. 8vo. 314 pp. Vienna. 1911. (German.)
- Human Food Materials; their Origin, History, Constituents, Use and Action. By C. HARTWICH. \$7.50. Leipzig. 1911. (German.)
- Influence of Low Temperatures (Frost) on the Strength of Mortar, Masonry and Concrete. By H. GEIMER. L. 8vo. 70 pp. \$1.50. Berlin. 1911. (German.)
- Safety Devices in Chemical Plants. By K. HARTMANN. \$4.50. Leipzig. 1911. (German.)
- RECENT JOURNAL ARTICLES OF INTEREST TO THE INDUSTRIAL CHEMIST.
- Chemistry and Technology of Petroleum for the Year 1910. By L. GURWITSCH. *Zeitschrift fuer angewandte Chemie*, Vol. XXIV, No. 27, pp. 1249-1256.
- The Acetylation of Cotton Cellulose. By CARL G. SCHWALBE. *Zeitschrift fuer angewandte Chemie*, Vol. XXIV, No. 27, pp. 1256-1260.
- Effect of Various Solvents on Sulfate Scale. By S. S. PECK. *International Sugar Journal*, Vol. XIII, July, pp. 357-359.
- Composition and Examination of the Residues from the Distillation of Fats. By J. MARCUSON. *Zeitschrift fuer angewandte Chemie*, XXIV, Heft 28, pp. 1297-1302.
- The Analysis of Manganese Bronze. By JAMES R. HUBER. *Metallurgical and Chemical Engineering*, Vol. IX, No. 8, pp. 403-404.
- Treatment of Anode Sludge in Electrolytic Refineries. By EDWARD F. KERN. *Metallurgical and Chemical Engineering*, Vol. IX, No. 8, pp. 417-420.
- The Influence of Impurities in Oxygen when Used for Cutting Iron and Steel. By ALEX. E. TUCKER. *Journal of the Society of Chemical Industry*, Vol. XXX, No. 13, pp. 779-782.
- Observations on Cotton and Nitrated Cotton. By H. DE MOSENTHAL. *Journal of the Society of Chemical Industry*, Vol. XXX, No. 13, pp. 782-786.
- The Analysis of Shellac. By A. C. LANGMUIR AND T. S. WHITE. *Journal of the Society of Chemical Industry*, Vol. XXX, No. 13, pp. 786-789.
- The Viscosity and Fluidity of Emulsions, Crystalline Liquids and Colloidal Solutions. By EUGENE C. BINGHAM AND GEORGE F. WHITE. *Journal of the American Chemical Society*, August, 1911, pp. 1257-1275.
- A New Method for the Separation of Cerium. By C. JAMES AND L. A. PRATT. *Journal of the American Chemical Society*, August, 1911, pp. 1326-1330.
- Volhard's Method for the Estimation of Chlorin in Potable Waters. By A. T. STUART. *Journal of the American Chemical Society*, August, 1911, pp. 1344-1349.
- Some Advantages of the Graphic Method of Recording Results in Routine Analysis. By J. H. RUSSELL. *Journal of the American Leather Chemists' Association*, August, 1911, pp. 382-387.

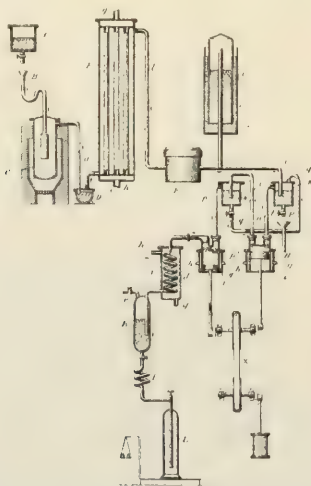
RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Method of Treating Distillation-gases to Produce an Illuminating Liquefied Gas.

U. S. Patent No. 994,369.

Satisfactory results are claimed to be secured by first compressing, after the usual cleaning, the distillation gas used for the purpose at a low stage of compression at normal temperature under water-cooling, then removing the liquid hydrocarbons thereby separated out, and compressing the so treated gas at the higher pressure necessary for its complete liquefaction, finally drawing it off into vessels of suitable material, such as steel. In this manner are avoided over-carburization of the gas and therewith subsequent separating out of fluid hydrocarbons and the loss occasioned thereby in the use of the gas.



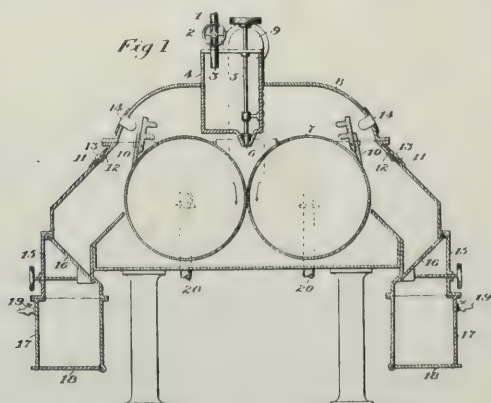
In the carrying out of the foregoing process the liquid hydrocarbons separated under pressure and saturated with gases under pressure should preferably be permitted to escape, at the pressure of the suction pipe, into a vessel inserted in the suction pipe of the apparatus or connected with the suction pipe by a gas-conduit pipe, in order to recover for the process gases set free from the fluid hydrocarbons through reduction of the pressure.

The accompanying illustration shows the apparatus in which the process is carried out.

Process of Desiccating the Solid Content of Milk.

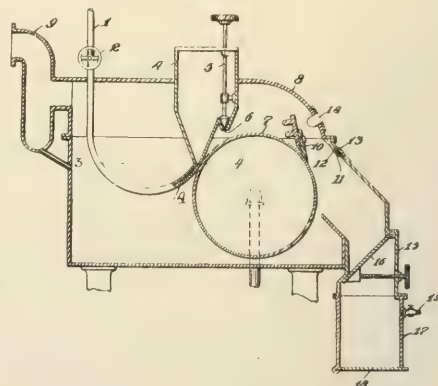
U. S. Patent No. 995,303.

The invention has for its object the separation of milk-solids in the form of a fluffy, flaky powder, which upon the addition



of warm water thereto will readily dissolve and emulsify to form a liquid having all the properties of normal milk. These objects the patentee claims to attain by delivering a mass of homogeneously-concentrated milk, free from unconcentrated portions in the form of a thin layer or sheet, to moving heated surfaces initially heated in excess of 5°C . above the boiling

Fig. 2.



point of the milk at the pressures at which the operation is performed. The layer is cooled during the formation of the same by the inflowing milk in its passage to the receiving receptacle, but without direct contact therewith and is removed in the form of a self-sustaining mass having the identity of a film from the heating surface prior to the complete evaporation of the water therefrom and while still possessing a slightly moist appearance.

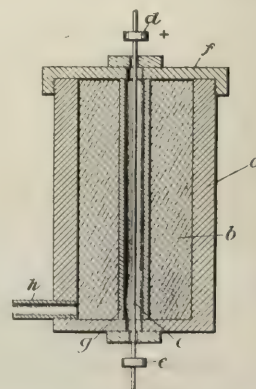
The accompanying illustrations show the apparatus in which the process is carried out.

The inventor is Waitstill H. Swenarton, of Montclair, New Jersey.

Method of Making Nitrogen Compounds.

U. S. Patent No. 996,011.

The method may be carried out by introducing into a suitable receptacle, constructed of material of low heat conductivity, provided with means for introducing nitrogen and containing electrical means of developing a temperature lying between dark red and light yellow, the desired quantity, say 100 kg., of finely



divided calcium carbide. This carbide may be ground to any suitable fineness. A small portion of the carbide immediately adjacent to the electrical heat-developing means is first raised to the temperature required to initiate the reaction at that point between the carbide and the nitrogen then or previously intro-

duced, and the process of conversion starts. The supply of nitrogen being maintained, the heat spontaneously resulting from the reaction between the carbide and nitrogen at this initial stage which we may call the ignition stage of the process is transmitted to an area still more remote from the ignition point and is sufficient to promote the reaction there; and so the reaction continues to spread until conversion of calcium carbide into calcium cyanamid is effected throughout the entire mass. This result will be recognized from the cessation in the consumption of nitrogen, which may be observed in any well-known manner.

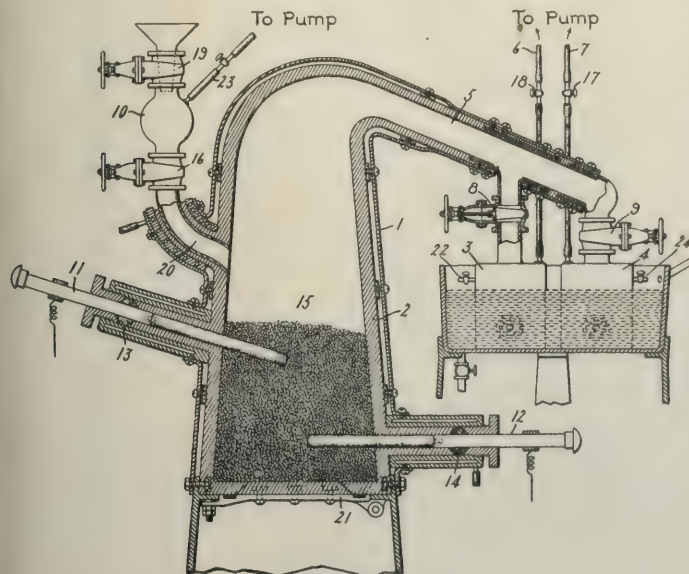
Referring to the accompanying illustration in which the figure is a diagrammatic sectional view of an apparatus suitable for carrying out the invention, *a* represents any suitable receptacle, *b* the material to be acted upon by nitrogen, *c* any suitable means for heating said material: for example, *a* resistor through which a current may be passed; *d* the positive terminal of a work circuit; *e* the negative terminal; *g* a tube or other receptacle through which the resistor *c* may pass; *f* any suitable closure for said receptacle; and *h* suitable means for introducing nitrogen gas.

The inventor is Albert R. Frank, of Halensee, near Berlin, Germany, assignor to Societa Generale Per La Cianamide, of Rome, Italy.

Fractional Distillation of Metals.

U. S. Patent No. 996,474.

The invention aims to provide certain improvements in the treatment of ores so as to effect a reduction of the ore and a purification of the product in one continuous operation. The process is defined in the patent as consisting in reducing the sulfid compound of a volatilizable metal by mixing said com-



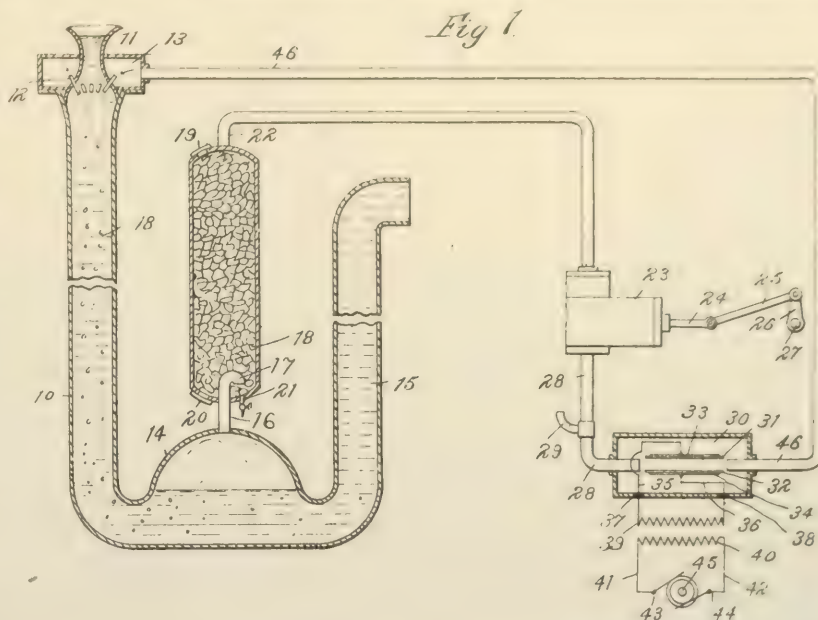
pound with a reaction material which will combine with the sulfur at an elevated temperature to form a relatively stable compound, heating said mixture to the reaction temperature and then removing the reduced metal from the by-products of the reaction by distillation in an attenuated atmosphere.

The inventor is Colin G. Fink, of Schenectady, New York, assignor to General Electric Company.

Apparatus for Purifying Water by Ozone.

U. S. Patent No. 996,560.

The object of the invention is to combine in a single system an efficient means for producing ozone, means for bringing the ozone



produced into intimate contact with the water to be sterilized and means for preparing air for ozonization. The inventor has combined a series of individual devices for performing the several features of the process each peculiarly adapted to its work in combination with the others so that the entire system or apparatus comprises a combination of elements, all coöperating to produce the desired result, and each one assisting the other in addition to doing its own work. In order to avoid the necessity of purifying too large a quantity of air, he has arranged and operates his apparatus in such a manner that the same air, or at least the greater portion of the same air, is used over and over again, only so much new air being admitted into the system at each cycle as will supply the required amount of oxygen to make up for the ozone which has been removed during the cycle by the oxidation of the carbonaceous impurities in the water being treated. In general the system may be described as comprising a water tower in which ozonized air is isothermally compressed by, and comes into intimate contact with, the water being treated; a separating chamber in which the air and ozone, together with the carbon dioxide and other obnoxious gases, are allowed to rise from the water; a lime chamber or tower into which the gases rising from the separating chamber are discharged and through which they pass and wherein the carbon dioxide is removed from the air; a compressed air engine suitably connected with the compressed air coming off of the lime tower and operated by the expansion of said air whereby the air is allowed to do work upon an operating shaft and is thus cooled and dried; and finally the ozone-producing apparatus into which the air thus cooled and dried is allowed

to pass for the purpose of having its oxygen converted into ozone. In addition to these general features the system comprises a suitable inlet for additional air which is supplied to the apparatus at each cycle to compensate for the ozone taken up by the carbonaceous impurities of the water.

The inventor is Charles S. Bradley, of New York, assignor to Richard B. Wilson, of that city.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF AUGUST.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Acetanilid.....Lb.	20 1/2 @	23
Acetone (drums).....Lb.	14 1/2 @	17
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	2.70 @	2.83
Acetic Acid.....C.	1.69 @	2.09 2/3
Aniline Oil.....Lb.	11 1/2 @	11 3/4
Benzoic Acid.....Oz.	11 1/4 @	12
Carbon Tetrachloride (in drums).....Lb.	8 @	12
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (in drums).....Lb.	12 1/2 @	14
Citric Acid (domestic).....Lb.	38 1/2 @	39
Camphor (refined in bulk).....Lb.		45
Dextrine (imported potato).....Lb.	5 1/2 @	7
Dextrine (corn).....C.	2.79 1/2 @	2.75
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....Lb.	20 @	21
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7 1/8 @	7 1/2
Pyrogallie Acid (bulk).....Lb.	1.25 @	1.55
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	2.02 1/2 @	2.18 1/2
Starch (potato).....Lb.	4 @	4 3/4
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 7/8 @	5 1/4
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	30 1/4 @	30 3/4

Inorganic Chemicals.

Acetate of Lime (gray).....C.	1.87 1/2 @	1.92 1/2
Acetate of Lead (brown, broken).....Lb.	7 3/4 @	8
Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (in drums) 16°.....Lb.	2 1/2 @	3 1/4
Ammonium Chloride, gray.....Lb.	5 3/4 @	6
Arsenic, white.....Lb.	17 1/8 @	2 3/8
Ammonium Carbonate, domestic.....Lb.	8 @	8 3/8
Aluminum Sulphate.....Lb.	90 @	1 3/4
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 1/4
Barium Nitrate.....Lb.	5 1/2 @	6 1/2
Borax, crystals in bags.....Lb.	3 1/2 @	4
Boric Acid, crystals.....Lb.	7 @	7 1/2
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.17 1/2 @	1.25
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 1/2 @	4 3/4
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	94 @	96
Chalk (light precipitated).....Lb.	4 1/2 @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (in bags).....C.	60 @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 1/4 @	8 1/2
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	81 @	84
Nitric Acid, 36°.....Lb.	3 7/8 @	4 1/4
Nitric Acid, 42°.....Lb.	4 7/8 @	5 1/2
Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25

Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 3/8 @	11
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals.....Lb.	8 1/4 @	9 1/2
Potassium Nitrate (crude).....Lb.	4 1/2 @	4 3/4
Potassium Bichromate, 50°.....Lb.	7 3/8 @	7 3/4
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	68 2/3 @	70 2/3
Salt Cake (glass-makers).....Lb.	62 1/2 @	77 1/2
Silver Nitrate.....Oz.	34 @	36
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 1/4 @	5
Sodium Chlorate.....Lb.	8 1/4 @	9 1/2
Sodium Bicarbonate (English).....Lb.	2 3/4 @	3
Sodium Bichromate.....Lb.	5 3/8 @	5 3/4
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 1/2
Sodium Hydroxide, 60 per cent.....C.	1.80 @	1.85
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.		7 1/4
Sodium Nitrate, 95 per cent., spot.....C.	2.12 1/2 @	2.15
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 3/4 @	10
Strontium Nitrate.....Lb.	7 1/4 @	8
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	85 @	1.00
Talc (American).....Ton	15.00 @	20.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	13 1/4 @	13 1/2
Tin Oxide.....Lb.	45 @	47
Tin Chloride (36°).....Lb.	11 @	11 1/2
Zinc Chloride (granulated).....Lb.	4 1/2 @	4 3/4
Zinc Sulphate.....Lb.	2 1/4 @	2 1/2

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 1/2
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	9 @	20
Corn Oil.....C.	6.06 2/3 @	6.11 2/3
Cottonseed Oil (crude), f. o. b. mill.....Gal.	38 @	40
Cylinder Oil (light, filtered).....Gal.	19 1/2 @	20
Japan Wax.....Lb.	9 @	9 1/4
Lard Oil (prime winter).....Gal.	78 1/3 @	85
Linseed Oil (raw, city).....Gal.	83 @	84
Linseed Oil (double-boiled).....Gal.	90 @	91
Paraffine Oil (high viscosity).....Gal.	23 1/2 @	24
Paraffine (crude 120 @ 122 m. p.).....Lb.	3 @	3 1/4
Paraffine (refined, domestic) 120 @ 122 m. p.....Lb.	4 1/2 @	4 3/4
Rosin Oil (first run).....Gal.	— @	37
Spindle Oil, No. 1.....Gal.	14 @	14 1/2
Stearic Acid (double-pressed).....Lb.	9 1/2 @	9 3/4
Sperm Oil (bleached winter) 38°.....Gal.	82 @	85
Tallow (acidless).....Gal.	64 @	66
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum [No. 1 ingots].....Lb.	20 @	20 1/2
Antimony.....Lb.	— @	8
Bismuth.....Lb.	— @	1.80
Copper (electrolytic).....Lb.	12.40 @	12.45
Copper (lake).....Lb.	12 3/8 @	12 3/4
Lead.....Lb.	— @	4.50
Mercury.....Lb.	61.3 @	61.5
Nickel.....Lb.	40 @	50
Platinum (refined).....Oz.	43.50 @	45.50
Silver.....Oz.	52 3/4 @	53
Tin.....Lb.	— @	43.43
Zinc.....Lb.	— @	5.95

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EDITORIALS

THE CONSERVATION OF RESEARCH.

The presidential address of Sir William Ramsay before the British Association for the Advancement of Science at its eighty-first annual meeting is rich in suggestions of great and important problems for scientific research and development, and also points directly at some of the issues of so-called conservation.

Sir William declared that if the stored-up energy in a ton of radium could be utilized in a space of thirty years instead of the inevitable period of 1,700 years, it would propel a 15,000 ton ship with a force of 15,000 horse-power at the rate of fifteen knots during the entire thirty years.

This prospect, however, is dimmed by the fact that the production of radium does not exceed half an ounce a year.

The study of radium and its compounds has finally led Madame Curie to establish beyond a doubt its identity as a chemical element which conforms to a position in the periodic system under barium. The establishment of radium as an element and the determination of its atomic weight and periodic relations are important matters from a chemical standpoint. These discoveries are also important from the standpoint of establishing a foundation upon which further researches into the peculiar properties of this element may be undertaken.

The potential possibilities of radioactive substances with stored-up energy and the transmutation inclinations displayed by them and their associates will always be an inviting field for research. Some of this research will be inspired by purely scientific motives; some by commercial needs. We may rest assured that all these research results will be exploited by the promoters and amateur conservationists.

Turning to the more directly practical subject of

energy from coal, Sir William declared that if the rapid increase in the output of coal mined in the British Isles continued, the supply would be exhausted in a hundred and seventy-five years—a very brief space in a nation's life. He urged that the present reckless waste should be discontinued and that every possible means of economizing should be adopted. Specific suggestions for its conservation were the use of turbines, gas engines, creation of power at the pit mouth and its distribution electrically, the abandonment of wasteful domestic fires in open hearths and the substitution of central heating plants. He even went so far as to recommend legislation to control the expenditure of the nation's fuel supply.

The conservation of the coal pile is as important to America as it is to Great Britain. It is important to the factory manager from the standpoint of economy in production, important to the mine owner from the standpoint of permanence of investment, and important to humanity at large if they have a regard for the future.

These and many other reasons make improvement in coal economy an important field for research.

The resources of chemistry and physics alone will not produce the highest attainable efficiency in the conservation of coal. Many worthy inventions fail through faulty business administration, so it appears that humanity is not doing its best with the administration of knowledge placed at its disposal for the conservation of the world's fuel supply.

It is an easy matter to show the loss in energy in converting coal into power or light, but how about the loss due to failure to utilize the natural power facilities of the country which eliminate the use of coal altogether?

The conservationist who "protects" a great waterfall from being utilized for producing power does not

consider the function of power and its relations to the great problems of conserving the fuel supply and the industrial development of the country. He does not understand industrial economics and its relation to human wealth, life and comfort, and may even be suspected of not understanding conservation.

Conservationists may be divided into two classes: sentimental conservationists and scientific conservationists. The loudest of these is the sentimental conservationist.

The ruins of the Temple of Philae were "saved" at the expense of an increased capacity of the Assuan dam which would have irrigated and rendered fertile and productive thousands of acres of the Nile Valley, to the great relief of an impoverished nation and race. Great waterfalls are "protected" at the expense of our coal deposits and power-using industrial enterprises.

The warnings of the scientific conservationists like Sir William Ramsay, are usually ignored and the scientific facts they adduce are swept aside by the impassioned eloquence of the sentimental conservationist or reformer.

While the chemical and physical investigator is working with unselfish devotion to solve problems which will conserve the world's resources for the benefit of mankind, why should not the people entrusted with the administration of the results of these investigations conserve them on a basis of scientific facts unmixed with sentimentality?

A workman with a bed, a bath, and a steady job is infinitely more important to humanity and to industry, and more inspiring to look at than a decayed temple. A factory using natural power and furnishing employment for hundreds of men and women under clean, light, sanitary conditions is certainly a better example of proper conservation of the researches of science than the dissipation of thousands of horse-power of energy by the reservation of a waterfall to satisfy the gaping curiosity of a few tourists.

THE RELATION OF CHEMISTRY TO HIGHWAY ENGINEERING.

Until very recently there has been but little need upon the part of highway engineers to call upon the chemist for aid in the science of road building. Earth, gravel and broken stone had been for many years practically the only materials necessary to successfully meet the requirements of country and suburban traffic, and previous experience had shown that the chemical analysis of these materials was of but slight assistance in determining their value for practical work. With comparatively few exceptions, highway engineers in this country had received little or no scientific education in road construction, and the few highly trained men engaged in such work found that sufficient information regarding the properties of materials employed could be obtained from a few simple physical tests and the use of the microscope. A very small number of chemists were en-

gaged in investigating the reason why certain classes of rock proved to be better road materials than others, when physical properties alone would not explain matters, but such work was in no sense of a commercial nature and was conducted almost exclusively in government laboratories.

These conditions maintained until a few years ago when the constantly increasing use of motor vehicles caused the subject to be considered from an entirely different point of view. The rapid destruction of many of our best and most carefully built macadam roads soon proved that broken stone as previously used was inadequate to meet the requirements of this new kind of traffic, and highway engineers found themselves confronted with a very serious problem. The rock dust necessary to bond together the coarser fragments of the macadam road, and preserve its integrity, was being removed by the passage of every automobile and this dust becoming a nuisance to those who used and lived near the road caused an insistent demand from the public not only for more lasting roads but for dustless roads as well. The highway engineer was thus forced to search for new materials of construction. After much experimenting he has found that the conditions of modern traffic may be successfully met by employing a variety of substances as binders for the road materials previously used. These new substances he has termed "dust preventives" and "road binders." The great majority of these materials come under the classification of bitumens, but a number of cheap by-products from various industrial sources have also been utilized for this purpose. Most of these dust preventives and road binders are extremely variable in composition and it has become practically impossible for the modern highway engineer to intelligently conduct his work without the assistance of the chemist.

The field thus opened is practically a new one in chemistry, although in its broadest sense it includes the chemistry of paving materials as practiced in connection with municipal work. For the purpose of illustrating the wide scope of this new field, some of the more important materials may be mentioned. These consist of petroleums and petroleum products, including residual petroleums, fluxes, oil-asphalts, and fluxed or cut-back oil asphalts; malthas; native asphalts and other solid native bitumens and asphaltic cements produced by fluxing them; coal tars and water gas tars, their distillates and residues; mixtures of tar with petroleum or asphalt products, bituminous emulsions, and fictitious asphalts; bituminous aggregates, including rock asphalts or bituminous rocks, bituminous concrete and asphalt or other bituminous topping; waste sulphite liquors; sucrares of certain inorganic bases; soluble silicates; calcium and magnesium chlorides; and various organic by-products from industrial processes.

The most important class of materials at present, the bitumens, alone offer an inexhaustible field of research in connection with their utilization in road construction. These products must be considered and examined as they exist and as they are offered

by manufacturers. It is true that the immense amount of study accorded this class of materials by chemists throughout the world is responsible for a very large portion of our knowledge of organic chemistry, but most of the work so far accomplished has been devoted to the isolation of certain organic compounds present in the crude material or to the preparation of new compounds, and this work is of little value in the field mentioned, which is obliged to deal with an endless variety of the most complex mixtures, solutions and emulsions of hydrocarbons and their derivatives, many of which are unstable and are undergoing constant changes, which affect their value as road materials.

Comparatively few chemists have as yet entered this field and those who have so far obtained recognition for their work might almost be counted on the fingers of both hands. Methods of examination and analysis at present employed are more or less crude, and a vast amount of work will be necessary to establish this branch of chemistry upon a satisfactory basis. The field is a most important one, however, and should prove attractive to many chemists and chemical engineers for whom it will most surely offer employment in the near future. Already its importance has been recognized by highway engineers of this and all of the progressive European countries as evidenced by the proceedings of the Permanent International Association of Road Congresses. The American Society for Testing Materials has established a Committee on the Testing of Road Materials, and the American Society of Civil Engineers has devoted much time and consideration to the subject. This branch of work will be recognized at the Eighth International Congress of Applied Chemistry under the section on Fuels and Bituminous Materials. Numerous chemical road material industries have recently sprung into existence, and many of those devoted to the manufacture of paving materials have widened the scope of their production to include various classes of dust preventives and road binders. Chemists are needed to control and perfect these processes, to inspect, analyze and specify products which are to be used and to carry on investigations relative to the utilization of by-products for road treatment and construction, to improve old and devise new methods of examination, and to determine the effect of certain constituents upon the value of materials for this work. Innumerable problems might be mentioned for the consideration of the chemist engaged in this line of work, for instance the effect of light, heat, and atmospheric exposure upon various types of bitumens, accurate quantitative methods for the determination of paraffin scale in native bitumens and of naphthalene in tars and tar products; an accurate quantitative method for separating tars from petroleum and asphalts in bituminous mixtures; a quantitative method for determining the presence of water gas tar in coal tar products, an absolute method for recovering bitumens unaltered from bituminous aggregates, and so on *ad infinitum*.

In order that the work of the chemist should be of

greatest value in highway construction, it is, of course, essential that he have a thorough knowledge of how the materials which he examines are actually used and what effect peculiar local conditions and conditions controlled by the highway engineer will have upon the results obtained in practice. In like manner it is necessary for the modern highway engineer to be informed in regard to the chemical and physical properties of the materials which he uses. During the coming winter a post-graduate course in highway engineering will be offered, by Columbia University, which will include instruction in the chemistry of road materials. It is therefore evident that the demand has already arisen for a new product of chemical and engineering sciences—"The Chemical Highway Engineer"—to whom the country must look for information and assistance in the intelligent expenditure of a vast amount of public money. This can best be realized from the fact that at the close of 1911 it is estimated that approximately one hundred and forty million dollars will have been spent by this country in the construction and maintenance of highways during the year and subsequent annual expenditures will probably far exceed this amount.

PREVOST HUBBARD.

INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

Tentative rules governing the presentation and publication of papers before this body at its meetings in September, 1912, have been issued, and in order that there may be no misunderstandings, all prospective authors should carefully read the rules that follow, submitting in writing any criticisms they may have to offer, together with suggested remedies for such criticisms.

1. All papers must be in duplicate and legibly written, preferably typewritten.
2. Each sheet must be written on one side only and *not* on both sides.
3. Each paper must be accompanied by an abstract thereof, also legibly written, preferably typewritten, and which must be in duplicate.
4. Papers and their abstracts, both in duplicate, must be in the hands of the American Committee not later than June 30, 1912. All papers received prior to that time and accepted will be printed in their respective Sectional Volumes and distributed to such of the attending members of the Congress as may desire them at or before the opening of the Congress. Papers received after that time, if accepted, will be printed, but may appear in an appendix which may or may not be ready by the opening of the Congress; the Congress cannot then undertake to print them along with the papers of those sections to which they may be assigned.
5. All papers or like contributions must be as concise as possible and must contain the full name and post-office address of their respective authors; further, what number, if any, of reprints of the paper or like contribution is desired.
6. Papers or other like contributions must be original and not elsewhere read or published, nor contributed

or offered to any other Society, Association or publication for presentation or publication. The offer of any paper to the Congress is a tacit and understood agreement to the foregoing requirement. No paper should deal with historical matter any more than is needful for a proper understanding of the new subject matter presented, which subject matter, as far as practicable, should be of a date subsequent to June, 1909, the date of the Seventh International Congress of Applied Chemistry, except by special request. Nonconformity to this requirement may be a reason for rejection; a remedy herefor is offered in paragraph 18.

7. All authors, as a matter of course, agree not to publish their accepted papers in any other publication except as hereinafter provided, and, further, they automatically agree to abide by any final decision of the Congress with respect to such paper or papers, their presentation, discussion or printing.

8. The Congress obligates itself to have its final Report and Proceedings, including subject and authors' index, completed and ready for distribution on or before December 31, 1912; in case those reports and proceedings be not ready for distribution by that date, authors of all papers received and accepted after June 30, 1912, may then publish in any journal or publication that they may elect. This refers only to the report and proceedings bound in paper; members desiring cloth-bound sets can obtain them at an advanced charge over the \$5.00 membership fee; such advanced charge will be announced later, but will probably be \$2.50; delivery of these cloth-bound sets will be about 90 days later than of the paper-bound sets. Authors of papers received before the close of June 30, 1912, may publish those papers in any publication they may elect after the paper is read or after the Congress has adjourned.

9. Authors of papers accepted and printed in full or in abstract will receive free of cost and all delivery charges, not to exceed fifty (50) reprints of each paper or abstract; additional copies of reprints can be had upon payment of the prices for such copies, which prices will be announced later. The Congress cannot undertake to furnish reprints of papers if the order for such reprints is not attached to the paper or abstract when received by the American Committee.

10. No paper offered to and accepted by this Congress can be at any time published elsewhere without giving credit to this Congress for such article or publication.

11. The Congress reserves the right to reject any paper or other contribution that may be offered to it.

12. Rejections by Sectional Committees will not be final; their decisions will be reviewed by the Committee on Papers and Publications, but rejection by that committee will be final.

13. Authors of finally rejected contributions will be notified in writing of such rejection immediately after it has been made, and, as far as the Congress is concerned, such final rejection is strictly secret and confidential.

14. Any paper which is of a pronounced polemical,

advertising or personal character may be thereby disqualified and for that reason alone rejected, regardless of whatever merit the paper may otherwise possess.

15. The Congress reserves the right to print the full paper only, or the abstract only, or the title only, in each case with the author's name and post-office address.

16. The Congress will not publish a list of rejected papers nor state what papers have been rejected; directly after the closing of the Congress all records relating to rejected papers and like contributions will be destroyed; any and all proceedings as to rejected papers or like contributions, so far as the Congress is concerned, will be strictly secret and confidential.

17. Authors are requested to state on the papers themselves their preferences for the sections in which they wish them to be read; the Congress will respect that request wherever practicable, but reserves the right to assign the paper to any other section that may be deemed more appropriate, and such disposition is final.

18. Authors will *not* receive printer's proofs of their papers or abstracts; nor will their papers or abstracts be revised after receipt by the American committees, except when express authority so to do is given in writing by the author and time and opportunity offer for such revision; authors of manuscripts so revised waive any and all right to complain of or rectify any such revision. (See paragraph 6.)

19. The time consumed in reading or presenting the substance of any paper by an author or his representative at a meeting of a Section must not exceed ten (10) minutes; papers or presentations requiring more time than that must be suitably condensed so as to fulfil that requirement.

20. Any one reading a paper of another's authorship must be fully equipped and prepared to defend the paper in discussion, and no one else will be permitted to read such a paper; an offer to read another's paper is an implied statement to the effect of such preparation.

21. In the absence of an author or his properly equipped representative the paper will be read by title only, and if there be any discussion it must be based upon the paper as printed, because neither the paper itself nor its abstract will be read; exceptions to this rule can be made only under regulations that may be adopted by each Sectional Executive Committee.

22. Discussions of a pronounced polemical, advertising or personal character may be ruled out by the Chair on that ground alone and not permitted to appear in the printed record; the ruling of the Chair in such matters is final and is not subject to revision or appeal.

23. Participants in discussions will be given an opportunity of editing the manuscript reports of their remarks, but printer's proofs will not necessarily be

submitted to them, although wherever practicable they will be so supplied.

It is contemplated to announce the final and definite rules governing the subject matter of this summary during December, 1911; criticisms received before December 1, 1911, will be duly considered.

ORIGINAL PAPERS.

THE DIRECT PRODUCTION OF MOLYBDENUM STEEL IN THE ELECTRIC FURNACE.¹

By E. T. DITTUS AND R. G. BOWMAN

Received October 1, 1911.

PREFACE.

It is the intention of the authors to present in the following paper a brief résumé of the properties, uses and methods of production of molybdenum steel, and to describe in detail a series of experiments on the production of molybdenum steel, direct from iron ore and molybdenite, in the electric furnace.

The use of a sulphide ore of so active a metal as molybdenum in connection with the manufacture of steel presents a number of problems. Foremost among these are the complete reduction of the molybdenum without serious loss, the diffusion of the molybdenum through the steel to form a homogeneous product and the elimination of the sulphur from the steel. The process employed was one based on a reaction described by F. M. Becket in U. S. Patent 855,157, and is believed to be new.

The authors wish to express their hearty appreciation and thanks to Professor W. G. Haldane and others for the encouragement and assistance they have given in carrying out the experimental investigations.

The desirable properties of molybdenum steel and the expense involved in its manufacture by the methods at present in use, led the authors to search for some reaction upon which could be based a process for its direct production from its most common ore. Without such a process any extended use of molybdenum steel, instead of tungsten steel, is very improbable. The reaction described by Becket appeared the most simple and was, therefore, made the subject of the investigations.

The production of steel direct from ore in the electric furnace is easily accomplished where the ore is pure. Certain impurities, particularly sulphur, are, however, very difficult to remove from the metal. Small amounts may be removed by the use of a basic slag but this method is limited in its application since the fusibility of the slag decreased rapidly with increasing basicity. For the reduction of molybdenite in the presence of molten iron it is necessary to have present some substance which has a greater affinity for sulphur than either molybdenum or iron. The compound formed by the desulphurizing agent and the sulphur must either pass into the slag or be volatilized as soon as formed. The two metals which seem best adapted for use as desulphurizers, under these conditions, are manganese and silicon.

¹ Paper presented at the General Meeting of American Electrochemical Society, Toronto, Sept., 1911.

The final rules so adopted will be published in the four official languages of the Congress, and will then be binding on all contributors to the Congress, and all papers offered to the Congress must be offered subject to those rules.

Manganese in the form of metal or as the ferro alloy reacts with sulphides at high temperatures according to the following reaction:



The manganese sulphide forms a slag resembling iron sulphide. If the above reaction takes place in a bath of molten steel or iron the resulting metal is apt to contain small included masses of manganese sulphide. Sulphur in this form has little effect on the properties of steel. This reaction might be applied to the production of alloy steels, such as molybdenum steel, by adding a mixture of molybdenite and ferro-manganese to the bath of molten steel just before tapping. This would result in the formation of ferro-molybdenum and manganese sulphide, the former alloying with the steel and the latter passing into the slag.

Silicon reacts with sulphides to form silicon sulphide SiS_2 and liberates the metal of the original sulphide. This is the reaction described by Becket.² The reaction has been investigated by Fielding³ who produced a yellow powder which sublimed at 1500°C . and which decomposed water with the formation of H_2S and silicic acid. This compound did not correspond to the formula SiS_2 . Sabatier³ describes a somewhat similar compound and suggests the formula Si_2S_4 . The heat of formation of SiS_2 is given by Sabatier³ as $+40.4$.

This reaction might be applied to the production of molybdenum steel in the same manner as the manganese reaction described above. The silicon, in the form of ferro-silicon, and the molybdenite should be reduced to powder, intimately mixed in the proper proportion to produce the reaction and added to the steel in the furnace before tapping. The mixture might be added in a soft iron tube or in small briquettes made up with a binder of sodium silicate. Addition in the ladle during tapping would probably result in raising the sulphur content of the metal on account of the absence of slag, which in the furnace would remove small amounts of sulphur which might tend to pass into the steel.

EXPERIMENTAL WORK.

The experimental work of this thesis was undertaken with a view to determine the feasibility of applying the Becket process to the production of molybdenum steel direct from iron ore and molybdenite in the electric furnace. The problems presented were: first, the design and construction of a suitable furnace; second, the production of a carbon steel by

² *Elec. Chem. and Met. Ind.*, Aug., 1909.

³ *Bull. de Soc. Chim. Paris*, 2, 38, 153.

³ *Compt. rend.*, 90, 819.

direct smelting from iron ore; third, the addition of molybdenum to the steel and the elimination of the sulphur of the molybdenite from the bath of metal. Of these the third presents by far the greatest difficulty.

FURNACE.

To accomplish the results desired it was necessary that the furnace fulfil the following requirements: the crucible walls should be of a neutral or basic material, free from carbon; the furnace should be easily charged and operated; the electrodes should be capable of a variety of adjustments; the furnace should be capable of being readily dismantled for the purpose of relining or making alterations. Since the best method of heating could be determined only by experiment, it was thought best to design a furnace capable of being operated as a Girod, or with slight alteration, as a Héroult furnace.

With the above-mentioned requirements in view, two furnaces were designed. These were essentially the same in principle but differed in the proportions of the crucible and in certain minor details. A detailed description of the design illustrated in Fig. 1 will suffice, since this was the furnace finally adopted and used in the investigations.

The crucible is elliptical in cross section and measures 6 inches \times 9 inches \times 8 inches (15 \times 23 \times 20 cm.) deep. The total volume of the crucible is about 360 cubic inches (5.5 liters), the volume of the smelting zone about 90 cubic inches (1.4 liters). The walls have a slight bosh to effect a concentration of heat at the base of the crucible. The crucible lining is of burned magnesite obtained by crushing magnesite brick to pass 10 mesh (2.5 mm.). The magnesite was mixed with tar to form a paste and rammed in hot around a central wooden form. The tar was burned out in the heating up of the furnace.

The walls are built up of eight fire-brick sections of special design, luted together with fire-clay and encircled by steel bands. These rest on a foundation

made up of two courses of standard fire-brick, with the joints filled with fire-clay.

The cover for the crucible is a solid elliptical fire-brick section 17 inches \times 20 inches and 2½ inches (43 \times 50 \times 53 cm.) thick, encircled by a steel band. The electrodes enter through the slot in the center of the cover. This slot admits of considerable lateral or angular movement of the electrodes. The under side of the cover is slightly concave. An asbestos gasket is placed under the cover where it rests on the top of the furnace, and small asbestos washers encircle the electrodes where they pass through the cover.

The tap-hole is 1¼ inches (3 cm.) in diameter, and is well rounded at its point of entrance to the crucible. A small hole 1 inch (2.5 cm.) in diameter extends diagonally from the top of the outer wall to the smelting zone for the purpose of pyrometer readings and for the escape of gases.

ELECTRODES.

The hearth electrode consists of six ½-inch (1.3 cm.) rods of Swedish iron screwed into a ⅜-inch (0.9 cm.) plate of the same material. The plate is embedded in the lining of the bottom of the crucible in such a position that the upper ends of the rods are flush with the inner surface. A copper strap ⅜ inch (0.5 cm.) thick and 1.5 inches (4 cm.) wide, bolted to the plate, extends outside the furnace for connection to the source of current.

The two movable electrodes are supported on a frame above the furnace. The supporting frame is entirely independent of the furnace proper and is therefore unaffected by expansion or contraction of the walls. The electrodes are cylindrical graphite rods 1.25 inches (3 cm.) in diameter and 11 inches (28 cm.) long. Each electrode is attached to a brass rod by means of a collar clamp and cotter pin. The rod carries a rack which meshes with a pinion mounted on the electrode support. The electrode supports are mounted to slide from right to left on the supporting frame.

This facilitates adjustment of the electrode while the furnace is in operation, and also allows the electrode to be pushed back out of the way when relining the crucible. The support is so constructed that the electrode may be swung about it as a center and inclined at any angle. Ordinary pipe fittings were used as much as possible in the construction of the frame and supports, since these give a light, strong construction, and require no special castings or forgings. An electrode support built entirely of pipe and fittings is illustrated in Fig. 2.

The furnace illustrated in Figs. 2 and 3 differs from that described above in having a crucible of double the depth described, *i. e.*, 16 inches (40 cm.), and a different arrangement of the rods in the bottom of the crucible. This furnace was designed to operate continuously with a column of cold charge resting on the molten material, as in a shaft furnace.

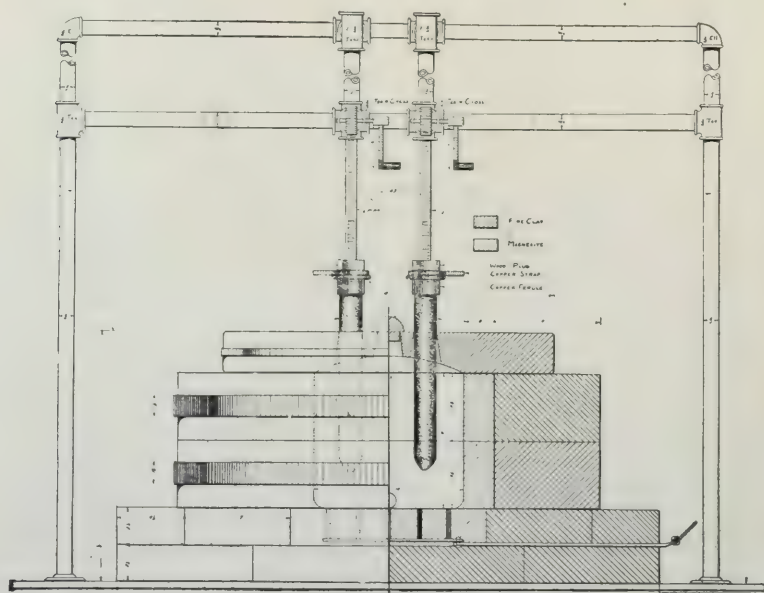


Fig. 1.

This type of furnace may be operated as a Girod steel furnace by connecting the two movable electrodes in parallel with one side of the circuit and the hearth

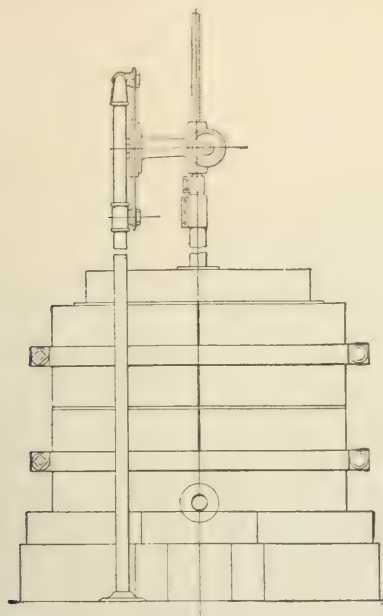


Fig. 2.

electrode with the opposite side. The movable electrodes may then be placed parallel vertically, thus forming two arcs, or set to converge to a single central point forming but one arc. To operate the

furnace as a Héroult steel furnace, the points of the rods in the hearth electrode are covered with a layer of magnesite, and the two movable electrodes are connected in series with the circuit. The magnesite covering for the hearth electrode need not be of any great thickness, since there is but a slight tendency for the current to cross through the iron plate after the charge becomes molten.

RUNNING OF THE FURNACE.

The furnace is charged at the beginning of a run by removing the cover and distributing the charge with a trough or funnel. Additional material may be added through the opening in the cover while the furnace is running.

The small amount of coke in the charge used was found to be sufficient to make the cold charge slightly conducting, the resistance rapidly decreases with rise of temperature, and the furnace may thus be readily started on a cold charge, providing the walls of the crucible are hot. The electrodes are forced down through the charge to within a short distance of the bottom of the crucible at starting. As the charge becomes hot, the electrodes are gradually raised until the charge is reduced and the arcs play between the ends of the electrodes and the surface of the slag. With the current available it was found impossible to maintain arcs below both electrodes simultaneously for any length of time. The best results were obtained by raising and lowering the

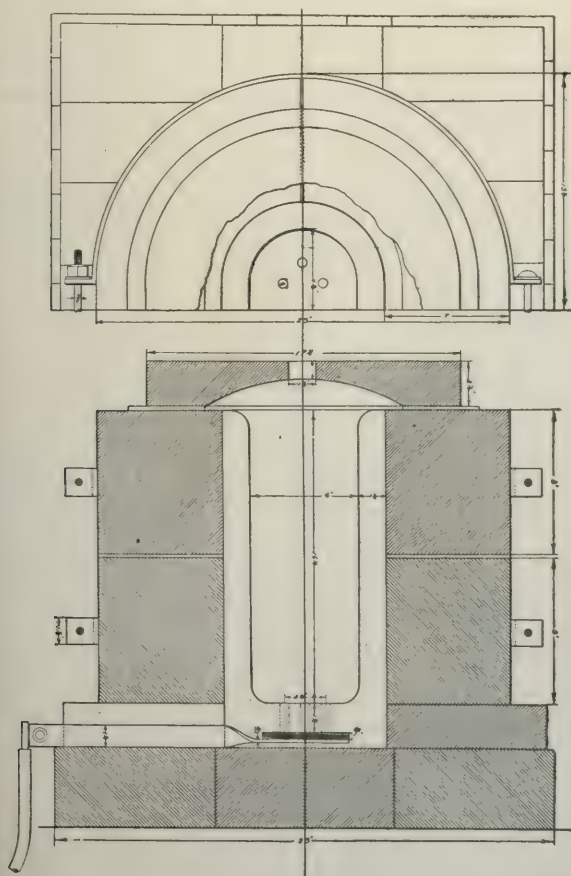


Fig. 3.

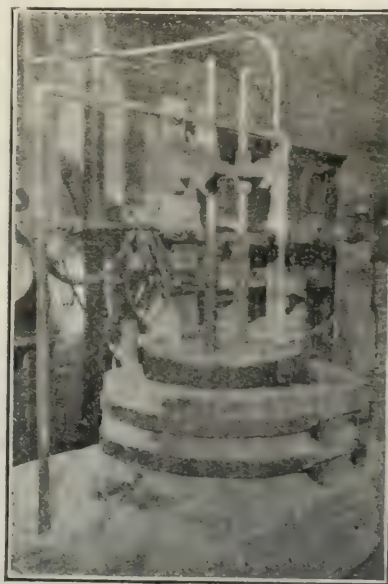


Fig. 4.

electrodes alternately at intervals of two or three minutes, which caused the arcs to alternate from one electrode to the other.

The capacity of the furnace as described is about 1000 grams of metal per charge, or approximately 2000 grams of raw charge. A charge of 1000 grams was employed in several runs. This yielded 500 grams of metal, but this amount is too small to make clean tapping possible.

Single-phase alternating current at 60 cycles, 25

volts, was employed. The amperage varied throughout the run, but averaged 250 with the arcs running steadily.

An opening for pyrometer readings was provided in the furnace, but no readings were taken. In a furnace of this size a variation of temperature from cold ore to the maximum smelting heat may be found in a space of a few inches; such a variation would make pyrometer readings irregular and of little value.

The generator used in supplying current for the experiment was a General Electric alternating current composite-wound, having both slip rings and a rectifier commutator for supplying direct current to the series

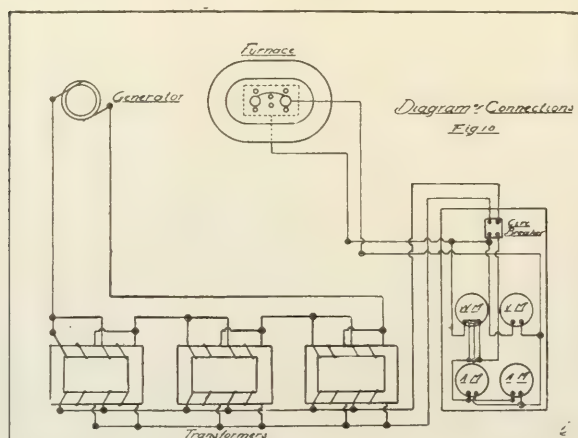


Fig. 5.

field. The name plate gives the following data: No. 2044, Type A, Class 10-30-1500. No load voltage 1040, Full load voltage 1155, Thompson-Houston System.

The transformers were made by the General Electric Co. No. 423,052, Type H, Cycles 60, Form G, Volts 1200, 2400, 120,240. The transformation ratio was 10-1. The primaries were connected in series with the line and the two coils in parallel with each other, the secondaries all in parallel with the line. This combination gave the best results. The amperage ranged from 0-500 with an average of 250, the voltage averaged 25.

The switchboard consisted of two ammeters in parallel with each other and in series with the line, a voltmeter in parallel, a circuit breaker, and recording wattmeter. The ammeters were made by Westinghouse Electric Co., 7,200 alt. circuit, cap. 300 amps. The voltmeter was a Thompson Portable machine, the circuit breaker an I. T. E. type W. 500 amps. The wattmeter was a Thompson recording, No. 104,114, Type M, Class 100-200 Form D₃.

During all the work the generator was run with the series coil short-circuited across the brushes. This protected the machine because any overload or short would cause the voltage to drop due to the armature reaction and reactance. A dead short would thus cause the voltage to drop to zero and thus no harm could be done to the machine.

The connections of the various pieces of apparatus are illustrated in the accompanying diagram (Fig. 5).

ORES AND FLUXES.

The iron ore employed was a good grade of hematite from the mines of the Colorado Fuel and Iron Co. at Sunrise, Wyoming. Two separate lots were used, the analyses of which were as follows:

	Per cent.
Fe.....	66.06
Al ₂ O ₃	1.52
SiO ₂	4.12
P.....	0.04
S.....	0.04

The ore was crushed to pass eight mesh (3 mm.) and the fines were retained.

MOLYBDENITE.

A quantity of very pure molybdenite from Yorkés Peninsula, Australia, was obtained from the Foote Mineral Co.

Analysis showed the material to be practically pure MoS₂ with only a trace of impurity in the form of copper sulphide.

FERRO-SILICON.

Two lots of ferro-silicon were used, the analyses of which were as follows:

	Per cent.
Fe.....	49.70
Si.....	50.00
S.....	0.005
C.....	0.20

The ferro-silicon and molybdenite were ground to pass thirty mesh (0.85 mm.) and intimately mixed in the proper proportions to bring about the reaction



The proper amount of this mixture to give the desired molybdenum content in the steel was enclosed in a small paper tube and added to the bath of metal just before reduction was complete.

COKE.

The coke used was from Trinidad, Colorado, and was obtained from the North American Smelting Co., of Golden, Colorado, from whom the analysis was also obtained.

Analysis:

	Per cent.
Fixed carbon.....	77.70
Vol. and combust. mat.....	2.80
Ash.....	18.66
Fe ₂ O ₃	1.23
Al ₂ O ₃	1.41
CaO.....	1.30
SiO ₂	6.59
S.....	0.47
Moisture.....	0.84

The coke was crushed to pass eight mesh (3 mm.) and the fines retained.

LIME.

Ordinary builders' lime was used as flux. The analysis was as follows:

	Per cent.
CaO.....	92.76
MgO.....	...
Fe ₂ O ₃ , Al ₂ O ₃	1.90
SiO ₂	1.34
P.....	0.96

The lime was crushed to pass eight mesh (3 mm.) and the fines retained.

RECORD OF FURNACE RESULTS

RUN NO. 5.

Charge:

Iron ore.....	3,025 gm.
Coke.....	660 gm.
Lime.....	412 gm.
Calculated iron content.....	2,000 gm.
Length of run.....	1 hr. 30 min.
Mean amperes.....	200
Mean volts.....	25
K. W.....	5
Metal obtained.....	1,700 gm.
Calculated molybdenum content.....	2.5 per cent.

Iron turnings were spread over the bottom of the crucible and covered by a layer of coke, lime and silica to form slag and protect the iron. The metal melted in 25 minutes but was kept molten in the furnace for 15 minutes after fusion in order to burn out the tar from new portions of the lining. This metal was tapped cleanly and a charge sufficient for 500 grams of metal was added. This reduced in 20 minutes. Molybdenite-ferro-silicon mixture sufficient to give a content of 5 per cent. Mo in the metal was added in a paper tube just before reduction was complete. The tap hole was opened but the metal was level with the tap and only slag flowed out. The tap hole was again plugged and a charge sufficient to give 1000 grams of metal was charged.

Reduction was rapid and the charge was entirely reduced in 30 minutes. Molybdenite mixture sufficient to give a molybdenum content of 2.5 per cent. in the metal was added just before final reduction of the charge. Since the bottom of the crucible appeared to be sinking constantly, another charge equivalent to 500 grams of metal was added and reduced in 15 minutes. This gave a total of 2000 grams of metal (calculated) in the furnace, with sufficient molybdenum to yield 2.5 per cent. in the total.

The tap hole was opened and slag flowed out freely but no metal was obtained. The current was shut off and the furnace allowed to cool. A solid mass of metal level with the tap hole was found in the bottom of the crucible.

The furnace was taken down and the entire lining and bottom electrode removed. A solid mass of metal weighing 1700 grams was obtained. The metal was malleable and tough, and was broken with great difficulty. When broken across the center the fracture was very fine-grained and dense at the center of the mass and coarsely crystalline and full of small blow-holes at its outer edges.

A section of the central portion of the mass, polished and etched with picric acid, showed a network of a bright white constituent, probably a double carbide of molybdenum and iron. A section in the coarsely crystalline portion of the mass showed a coarsely granular structure.

Analysis:

	Per cent.
C.....	0.62
Si.....	0.91
Mo.....	1.15
P.....	0.08
S.....	0.37

RUN NO. 6.

Charge:

Iron ore.....	156 gm.
Coke.....	163 gm.
Lime.....	101 gm.
Calculated iron content.....	500 gm.
Calculated molybdenum content.....	2 per cent.
Length of run.....	30 min.
Mean amperes.....	300
Mean volts.....	25
K. W.....	7.5
Metal tapped.....	

Description of run:

The furnace was rebuilt and arranged as in Run 5. The tap hole was given a slightly greater inclination.

Iron turnings were placed on the bottom of the crucible and were melted in 30 minutes. The tar in the new lining burned out very slowly and the molten metal was, therefore, allowed to remain in the furnace for one and one-half hours with the arcs running. When the greater part of the tar was burned out the metal was tapped and the charge added.

Reduction was rapid and molybdenum mixture sufficient to give a molybdenum content of 2 per cent. was added. The walls of the crucible were crumbling and the crucible was rapidly becoming too large to heat properly. The magnesite from the lining made the fused charge thick and pasty. An attempt was made to tap the metal but nothing was obtained. The crucible was now too large to work properly but since the bottom seemed to be sinking it was thought advisable to fill the crucible up to the proper level by the reduction of a large charge of ore. A charge corresponding to 2000 grams of metal was added in small amounts with the arcs running. Reduction was rapid but not uniform, owing to the increased size of the crucible. By continual poking of the charge the whole mass was finally fused but was not sufficiently liquid to tap. The furnace was allowed to cool and a mass of metal level with the tap hole was found embedded firmly in the bottom. A small portion of this metal was removed with tongs and proved to be very soft and malleable and easily sawed or cut.

A polished section etched with picric acid showed a network of bright white lines in a ground of pearlite.

Analysis:

	Per cent.
C.....	1.14
Si.....	1.23
P.....	0.03
S.....	0.03
Mo.....	0.45

RUN NO. 7.

Charge:

Iron ore.....	1,512 gm.
Coke.....	326 gm.
Lime.....	206 gm.
Calculated iron content.....	1,000 gm.
Length of run.....	60 min.
Mean amperes.....	300
Mean volts.....	25
K. W.....	7.5
Metal tapped.....	

The crucible was relined. The electrodes were partially consumed and, since no more of the same

size were at hand, were removed and replaced by $1\frac{1}{8}$ inches (3 cm.) rods. The arcs were started on the mass of metal remaining from Run 6. When the furnace was hot and this metal was molten, a charge was added and quickly reduced. The tap-hole was opened, but only a portion of the metal was obtained. The charge was then found to have formed a scaffold across the crucible. It was found impossible to smelt down the semi-fused mass forming the scaffold with the small electrodes at hand; the furnace was, therefore, allowed to cool and the material picked out.

The metal obtained in tapping had a coarse crystalline structure and was extremely hard and tough.

A polished section etched with picric acid and magnified 180 diameters showed irregular branching figures of a bright white constituent in a ground of granular pearlite.

Analysis:

	Per cent
C.....	0.71
Si.....	2.14
(Large amount of scale in sample.)	
P.....	0.04
S.....	0.025
Mo.....	1.95

RUN NO. 8.

Charge:

Iron ore.....	1,512 gm.
Coke.....	326 gm.
Lime.....	206 gm.
Calculated iron content.....	1,000 gm.
Calculated Mo content.....	5 per cent.
Length of run.....	60 min.
Mean amperes.....	300
Mean volts.....	25
K. W.....	7.5
Electrode consumption.....	65.0 gm.
Metal tapped.....	

The furnace was started on a small amount of wrought iron punchings, covered by a little powdered coke. These melted rapidly, and a small charge was thrown in in small portions with the arcs running freely. When the metal was all melted, the entire charge was added and the electrodes embedded in the cold material. The small rods employed in Experiment 7 had been replaced by full-size electrodes.

Reduction of the charge was rather slow. At the end of sixty minutes an attempt was made to tap. Slag flowed out freely and filled the mould, but the metal would not flow. The tap-hole was closed and a strong arc started to melt the mass of metal. Upon tapping, a portion of the metal was obtained. This was tough and malleable and had a very fine-grained structure.

The molybdenum mixture was added as usual just before reduction was complete. When the arc was started on the surface of the metal after tapping the slag, a white sublimate formed on the electrodes and the under surface of the cover. This was probably MoO_3 , formed by the oxidation of the metallic molybdenum in the steel, which was unprotected by slag.

A polished section of the metal tapped, when etched with picric acid and examined under a magnification of 180 diameters, showed a coarse network of the characteristic bright white constituent in a mass of pearlite.

Analysis:

	Per cent.
C.....	0.92
P.....	0.043
Si.....	1.10
Mo.....	2.15
S.....	0.036

RUN NO. 9.

Charge:

Iron ore.....	756 gm.
Coke.....	163 gm.
Lime.....	103 gm.
Calculated iron content.....	500 gm.
Length of run.....	60 min.
Mean amperes.....	300
Mean volts.....	25
K. W.....	7.5
Metal tapped.....	
Calculated molybdenum content.....	0.6 per cent.

The furnace was started on the metal remaining in the crucible. When the crucible was well heated, the charge was added, and reduction was rapid. At the end of sixty minutes an attempt was made to tap. Slag flowed out freely, but the metal would not flow. This was due to a dam of metal formed just outside the tap-hole from a leak in the clay plug.

The furnace was allowed to cool, and a mass of metal weighing about 450 grams was taken from the crucible with tongs. This metal was very malleable and tough and could be easily sawed and cut.

A polished section, etched with picric acid and examined under a magnification of 190 diameters, showed the characteristic net-work of double carbide and in addition a mass of needles of a white constituent resembling the carbide.

Analysis:

	Per cent.
C.....	0.54
Si.....	1.65
Mo.....	0.45
P.....	0.07
S.....	0.05

RUN NO. 10.

Molybdenum steel from molybdenite concentrates.

Analysis of concentrates (Wood's Flotation Process):

	Per cent.
Mo.....	11.10
Cu.....	0.72
S.....	15.00
SiO_2	65.00

Molybdenum mixture (equivalent to 0.66 per cent. Mo in calculated iron).

	Grams.
Concentrates.....	100
Si-Fe.....	9.28
Lime.....	65.00

Charge:

As in previous runs, equivalent to 1500 grams calculated iron.

Length of run.....	40 min.
Mean amperes.....	250
Mean volts.....	25
K. W.....	6.25
Metal tapped.....	1,370 gm.

Furnace started on metal in bottom. Charge added in two portions and reduced rapidly. A tap was attempted after the addition of the first charge, but the metal would not flow. The molybdenum

mixture was added in two equal portions and was reduced almost instantly. The trap was clean and the ingot obtained was sound and free from large blow holes. The increase in molybdenum content in the metal over that calculated was probably due to a concentration of the molybdenum in the metal reduced.

A polished section, taken from the center of the ingot, when etched with picric acid and examined under a magnification of 180 diameters, showed a fine network of the double carbide and small isolated patches of the same constituent all in a ground mass of pearlite.

Analysis:

	Per cent.
C.....	0.70
SiO ₂	1.20
Mo.....	0.70
P.....	0.10
S.....	0.45

CONCLUSIONS.

Since the results of the experiments herein described, with the exception of runs Nos. 5 and 10, were qualitative rather than quantitative, further experiments would be necessary in order to determine the loss and distribution of molybdenum.

Since no analyses were made upon the slag, it is impossible to determine what proportions of the sulphur were removed by the ferro-silicon and the slag.

(1) Molybdenum steel can be made in the electric furnace by the direct reduction of iron ore and the addition of molybdenum in the form of molybdenite, MoS₂.

(2) Molybdenum steel of low sulphur content can be produced from molybdenite by the use of ferro-silicon as a desulphurizer.

(3) Molybdenum steel of low sulphur content can be produced from molybdenite in the form of low-grade concentrates by the use of ferro-silicon as a desulphurizer.

With regard to the design of a furnace for small scale operations, the foregoing experiments would indicate that:

(1) The Girod principle as used was superior to the Héroult.

(2) A tilting furnace would be more effective than a stationary furnace.

(3) The tap-hole on a stationary furnace should be made short, with a steep inclination. Ample provision for heating the tap-hole should be made.

(4) Tar does not make a satisfactory binding material for crushed magnesite.

COLORADO SCHOOL OF MINES,
GOLDEN, COLORADO.

CONCENTRATION AND PURIFICATION OF IRON ORE, HIGH IN SULPHUR, BY ROASTING IN A ROTARY KILN.¹

By JAMES OTIS HANDY AND JOHN M. KNOTE.

Received July 14, 1911.

While the amount of high-grade iron ore still unmined is vast in quantity, the deposits of lower grade

¹ Read by James Otis Handy at Indianapolis Meeting A. C. S., June, 1911.

are receiving serious attention. Water concentration, magnetic separation or roasting are being used as means of eliminating in part sulphur, phosphorus and silica and raising the iron content so that the ore becomes commercially valuable. This paper is concerned with the solution of a problem of concentration by roasting.

THE ORE.

The ore consisted of approximately the following mixture of minerals:

Magnetite (Fe ₃ O ₄)	32.6 per cent. = 23.66 per cent. metallic iron
Siderite (FeCO ₃)	27.1 per cent. = 13.50 per cent. metallic iron
Pyrite (FeS ₂)	7.5 per cent. = 3.50 per cent. metallic iron
Calcite (CaCO ₃)	13.2 per cent. = 7.4 per cent. calcium oxide
Magnesite (MgCO ₃)	10.8 per cent. = 5.1 per cent. magnesium oxide
Manganous oxide (MnO)	2.5 per cent. = 1.95 per cent. manganese
Silica (SiO ₂)	6.3 per cent. =

ANALYSIS OF CARGO SAMPLE.

	Per cent.
Iron.....	40.66
Manganese.....	1.95
Lime.....	7.40
Magnesia.....	5.10
Carbon dioxide.....	21.80
Alumina.....	1.25
Silica.....	6.32
Sulphur.....	4.01
Phosphorus.....	0.015

No doubt the carbonates of calcium and magnesium were combined as dolomite.

The advantage of the roasting process over other concentration processes was obvious; the valuable fluxing agents would be retained and if the expulsion of sulphur could be made complete enough, even the iron in the pyrite would be available.

LABORATORY EXPERIMENTS.

An average sample of the iron ore, obtained by diamond drilling, was used. It was crushed to pass a 1/2-inch screen. The first experiments were in roasting in a muffle furnace at a temperature of 650-750° C. which is usually considered favorable for the elimination of sulphur from pyrite.¹ Hardly more than 2 per cent. of sulphur (about one-half) could be roasted out at this temperature even when ore finer than 1/2 inch was used. The temperature was gradually increased with very slight gain until 1100° to 1150° C. had been reached when the sulphur percentage dropped rapidly from about 1 per cent. to less than 0.1 per cent. and in some cases the sulphur was entirely eliminated.

The most successful experiments were those in which the ore was introduced into a muffle having a temperature of 1150° C. The door was closed after 15 minutes. The heating then continued for an hour at a temperature of 1150° C. The ore had fused or sintered slightly, and contained from 0.032 per cent. to no sulphur.

Apparently it was necessary to raise the roasting temperature above the point where sulphates could exist or where lime could hold sulphur. Although the successful experiments with small lots of ore in a closed but not sealed muffle seemed to indicate oxidation of sulphur by oxygen in the ore itself, subsequent tests showed that half or less of the sulphur could

¹ Lunge, *Sulphuric Acid and Alkali*, 1, 1, 340 (1903).

be distilled off in the absence of air at 1150° C. or higher.

We found that muffle roasting with exclusion of products of combustion was not necessary. We made successful roasts in the presence of the products of combustion of natural gas, burned with the aid of an excess of air under pressure.

By our laboratory experiments we proved:

1. The normal roasting temperature for pyrite (650–750° C.) must be far exceeded. For sulphur elimination 1100–1200° C. was required.

2. The roasting could be done in the presence of combustion products at the required temperature if an excess of air were present.

3. The final expulsion of the sulphur took place at or near the sintering point of the ore.

These results were sufficiently encouraging to warrant experiments on a larger scale.

ROTARY KILN EXPERIMENTS.

A rotary kiln was chosen for this work because it had already been used commercially for nearly eliminating the 2 or more per cent. of sulphur left by H_2SO_4 manufacturers in their pyrites cinder. It was further recognized that the successful furnace must require little labor to operate. The laboratory experiments had shown that rotary cement kiln temperatures had not been exceeded, so that unless the sulphur oxidation were slower than the lime-silica-alumina reactions in the cement-kiln, the cost of roasting would not be too great.

The rotary kiln which was used was 70 feet long by 5½ feet inside diameter. It was lined with fire brick and was otherwise very similar to a cement kiln. The ore entered through a hopper at one side of the upper end and the combustion gases escaped at the opposite side of the same end. The pitch of the kiln was 1/2 inch per foot.

The kiln was fired with pulverized slack coal of the following composition:

ANALYSIS OF COAL USED.	
	Per cent.
Moisture.....	6.40
SAMPLE DRIED AT 100° C.	
Volatile matter.....	39.19 per cent.
Fixed carbon.....	50.84 per cent.
Ash.....	9.97 per cent.
Sulphur.....	4.29 per cent.
B. t. u.....	13285

The coal was reduced to powder and blown into the kiln by an Aero pulverizer, a combination of disintegrator and fan. It is not possible with this apparatus to control the quantity of air absolutely. It is difficult to maintain a uniform feed of uniformly pulverized coal. It has the advantage of being workable with moist coal while most other systems of firing require that the coal should be dry before it is reduced to powder.

The speed of revolution of the kiln was from once in 45 seconds to once in four minutes.

For the first two runs the ore was used as it was brought from the mines, and no further screening or crushing was done. For the remaining runs, screened and crushed ore was used. It will be seen

from a careful study of the results, that final success was not due, to any great extent, to the crushing of the ore. Coarse lumps were shown to be as completely desulphurized in the majority of cases as the fine ore at the same point in the kiln after the last run. In the case of runs 1 to 3 inclusive, the ore was allowed to pass completely through the kiln. In the case of runs 4, 6 and 8, the kiln was stopped as soon as the last of the ore had been charged into it, and samples were taken after the kiln had cooled, so that the progress of desulphurization could be carefully studied.

The ore was shoveled from the cars to a chute, leading to the bucket elevator. This elevator discharged, in the first two runs, directly into the hopper of the kiln. In the subsequent runs it discharged into rolls which dropped the ore to a second elevator, which conveyed it to the hopper of the kiln.

Samples were taken at the rate of one shovelful every five minutes. The samples thus taken were quartered and in four cases were sized to determine the percentage of each size. In the case of runs Nos. 1 and 2, the sizes were analyzed separately for sulphur, but as no significant difference was shown in the sulphur content of the different sizes, only average samples were analyzed thereafter.

The oversize in both cases we estimated would nearly all pass through a two-inch grill.

The ore contained very little moisture at the start and the weather during the test was favorable.

The problem was to determine under what conditions the sulphur in the ore could be reduced below 0.50 per cent. We wished to determine the following points:

- (1) Maximum permissible size of ore.
- (2) Maximum output of ore.
- (3) Most favorable speed of rotation of kiln.
- (4) Most favorable temperature and method of firing.
- (5) Fuel consumption per unit of ore roasted.

It was not possible with the plant at our disposal to determine all of these points, but much valuable information believed to prove the feasibility of commercial roasting was secured.

(1) *The ore size* was 2 inches and less in runs 1 and 2. In run 1 the kiln was too cold, and in run 2 too hot locally, but not hot enough in the upper part, so that the question of the effect of ore size was not settled by these runs. For run 8 the ore was screened through a 1½-inch but not further crushed. The success of run 8 leaves it beyond question that ore through 1½ can be successfully desulphurized. Some pieces 2 inches × 3 inches × 1½ inches were found in the kiln after run 8. They were in three out of four cases desulphurized to as great an extent as the average ore at the same point. This indicates that 1½ inches may not be the limiting size.

(2) *Maximum output of ore* could not be determined with a seventy-foot kiln under existing conditions. We believe, however, that six tons per hour could have been desulphurized to below 0.5 per cent. in run 2 if the kiln temperature had been kept up. Analy-

sis of sample No. 5 shows sulphur under 1.0 per cent. when the original mixture of coarse and fine ore was fed at the rate of six tons per hour.

(3) *Most Favorable Pitch and Rate of Revolution of Kiln.*—The result of run 1 does not show that one revolution in forty-five seconds was too fast. The low kiln temperature left the speed factor indeterminate. As the results stand we have proved that one revolution in four minutes will do the work and have made it seem probable that the speed used on run 2 (one revolution in one minute and 35 seconds) will not be excessive. The fact that coarse and fine ore came through with 80 per cent. of the sulphur eliminated at first, when the heat was high enough, shows what might have been expected with better heat distribution and maintenance.

At one cement plant, kilns $120' \times 7\frac{1}{2}'$ with a pitch of $\frac{3}{4}$ inch per foot are run at 1 revolution per minute.

At another cement plant, kilns $125' \times 7\frac{1}{2}'$ with a pitch of $\frac{5}{8}$ inch per foot are run at 0.6 revolution per minute.

At another cement plant, kilns $125' \times 7\frac{1}{2}'$ with a pitch of $\frac{1}{2}$ inch per foot are run at 1 to $2\frac{1}{2}$ revolutions per minute.

The tendency seems to be toward flatter pitch and higher speed.

(4) *Most Favorable Temperature and Method of Firing.*—This point we believe to have been completely covered by the last run, No. 8. This test showed that with a sufficient velocity and quantity of air the pulverized coal flame was a long oxidizing one, entirely adequate for complete desulphurization of the ore. In previous runs the flame had been either too hot, locally, or too cold and too reducing in character. In run 8, the kiln was heated quite uniformly for a distance of 40 feet, beginning at a point about 20 feet from the discharge end. The flue temperature six feet from the kiln was 1000°C . at the start and 980°C . at the finish. It fell to 950°C . only once for an hour or less. The temperature of the interior of the kiln we estimate to have been 1100 – 1200°C . for a distance of at least 30 feet.

With a longer kiln, or with a longer hood at the lower end of a seventy-foot kiln the gases would pass cooler to the chimney and greater fuel economy would result.

(5) *Fuel Consumption.*—Owing to the difficulties in determining the actual amount of coal consumed in the earlier tests, and to known excessive consumption in some of the later ones, we are not able to vouch for the fuel consumption figures. It is certain, however, that the consumption of fuel will not exceed that in cement manufacture, because in that case the temperature reached is 100 – 200°C . higher.

A 100-foot cement kiln 7 feet in diameter, putting out 375 barrels, equals 70.5 tons of cement per day, uses 115 to 125 pounds of coal per barrel or 31.9 per cent. of the cement produced.

A 125-foot cement kiln, 8 feet in diameter, putting out 600 barrels, or 112.8 tons per day, uses 25.3 per cent. of coal.

The minimum coal consumption in cement practice has approximated 19 per cent. in kilns $200' \times 12'$. The average is 23 to 24 per cent. in kilns 120 to 125 feet long by $7\frac{1}{2}$ by $6\frac{1}{2}$ feet inside diameter. It is believed that the fuel consumption in cement burning can be much further reduced.

The detailed data or log of each run, including chemical analyses of the ore used and the roasted ore produced, is given below.

RUN No. 1.—HIGH SULPHUR IRON ORE.

Nov. 22, 1910, 9.17 A.M. to 3.15 P.M. = 6 hours

Size of ore	Per cent.	Per cent. sulphur.	Per cent. sulphur
			Average.
on 1-inch screen	14.23	containing 4.42	4.19
on 1/2-inch screen	23.01	containing 4.09	
on 1/4-inch screen	20.65	containing 3.96	
through 1/4-inch screen	42.11	containing 4.27	

Rate of feed, 53,980 pounds of ore, or 26.99 tons in 6 hours, or 4.5 tons per hour.

Coal used, 3.46 tons or 12.8 per cent.

Rate of kiln rotation, 45 seconds.

Ore passes through kiln in 30 minutes, or at the rate of 2.33 feet per minute.

Ore feed started at 9.17 A.M. Ore all in at 2.45 P.M. All through at 3.15 P.M.

Flue temperature at point six feet from kiln, as follows:

9.07 A.M.	11.25 A.M.	11.45 A.M.	12 M.	12.10 P.M.	2.55 P.M.	3.02 P.M.
925°C .	780°C .	800°C .	793°C .	785°C .	820°C .	830°C .

Fuel used, 6,930 pounds coal, or 1,155 pounds per hour, or 12.8 per cent. of raw ore, or 16.0 per cent. of roasted ore.

Heat distribution was poor. Kiln temperature low.

The ore was rarely sintered. None was heated hot enough or long enough. Heat localized and insufficient.

Sample No.	Time.	Remarks.	Size. Inch.	Sulphur. Per cent.	Iron. Per cent.
1	10.25 A.M.	odor of sulphur dioxide	...	4.47	49.30
2	11.05 A.M.	slight sintering of fine ore	...	3.82	51.10
3	11.25 A.M.	slight sintering of fine ore flue temperature 780°C .	1	3.89	51.00
			$3/4$	3.45	51.10
			1/2	3.19	51.70
			1/4	3.35	51.50
			1/8	3.37	51.10
4	11.50 A.M.	Through	1/8	2.89	51.00
		good 1-inch nodules; flue 800°C	2.31	52.00
B-1		average of all roasted ores	...	2.46	...

Conclusion.—Kiln was hotter during last half of run. Sulphur must have been reduced below 2 per cent. as roasted ore averaged 2.40 per cent. Failure due to too cold kiln. Sulphur removal was 40 per cent.

RUN No. 2.—HIGH SULPHUR IRON ORE.

Nov. 23, 1910, 10.20 A.M. to 4.20 P.M. = 6 hours.

Size of ore	Per cent.	Per cent. sulphur.	Per cent. sulphur
			Average.
on 1-inch screen	47.48	containing 4.82	4.46
on 1/2-inch screen	17.83	containing 4.28	
on 1/4-inch screen	17.83	containing 4.09	
through 1/4-inch screen	16.86	containing 4.00	

Rate of feed, 6 tons per hour (10.20–11 A.M.), 3.6 tons per hour afterward.

Ore roasted, 43,640 pounds (approximately). Coal used, 6,650 pounds (approximately). Coal was 15.2 per cent.

Rate of kiln rotation, 95 seconds.

Ore passes through kiln in 1 hour and 10 minutes, or 70 minutes.

Rate of travel of ore, 1 foot per minute.

Flue temperature:

10 A.M.	11.10 A.M.	11.35 A.M.	12.26 P.M.	1 P.M.	3 P.M.	4 P.M.
910° C.	800° C.	760° C.	690° C.	700° C.	700° C.	750° C.

Kiln temperature at 1 P.M. (Féry pyrometer), hot zone 10' long, 12' from discharge end of kiln was 1250° C.

Fuel used, 10.20–5 P.M. was 6,650 pounds or 1,000 pounds per hour, or 13 per cent. of raw ore or 16.3 per cent. of roasted ore.

Heat distribution was poor. The hot zone was too hot so that the ore fused and formed a heavy ring.

The temperature generally, as shown by the flue pyrometer, was not hot enough.

Sample No.	Sulphur. Per cent.
5 11.30 A.M. First ore through before kiln cooled by ore	0.95
6 11.50 A.M. Flue temp. lower; odor of sulphur dioxide	1.66
7 12.15 P.M. First effect slower feed, but kiln cooling	1.91
8 12.45 P.M. Flue 690° C.; slight odor SO ₂	2.01
9 1.15 P.M. Ore viscous; too hot to roll; estimated 1300° C.	1.87
10 2.45 P.M. Slagged, melted material, estimated 1300° C.	1.72
11 3.30 P.M. Piece of ring removed while running	1.53
12 3.40 P.M. Ore back of ring. Estimated held there an hr.	1.33
13 3.30–4.30 P.M. Ore back of ring. Estimated held there 20 min.	1.64
B-2 Average of all roasted ore	1.70
14 Solid ore; ring 7 ft. in kiln after run No. 2	0.85
15 Porous ore from ring 17 ft. in kiln; part next lining	0.25
16 Solid ore on top of No. 15 sample	1.45

Summary.—Run No. 2, because of local overheat and general low heat, failed as a whole to remove over 60 per cent. of the sulphur. Sample No. 5, however, shows that with a feed of 6 tons per hour and the coarsest ore used in any run (47 per cent. on 1 inch), the sulphur removal corresponding to a flue temperature of 910° C. was nearly 80 per cent.

RUN NO. 3.—HIGH SULPHUR IRON ORE.

Nov. 25, 1910, 6.40 P.M.–11.45 P.M.

	Per cent. sulphur.	Per cent. Average.
Size of ore { on 3/4-inch screen	4.58	4.32
(screened after { on 1/2-inch screen	21.46	
being crushed) { through 1/2-inch screen	74.00	

Rate of feed, 4,520 pounds per hour. 22,600 pounds roasted.

Coal used, 5,880 pounds or 2.94 tons or 29.4 per cent. of the ore.

Rate of kiln rotation, 2 minutes and 20 seconds, or 140 seconds.

Ore passes through kiln in 1 hour and 15 minutes, or 75 minutes, or at the rate of 0.93 feet per minute.

Flue temperature:

6.40 P.M.	7.45 P.M.	8.30 P.M.	10.40 P.M.
815° C.	740° C.	735° C.	840° C.

Kiln temperature, hot zone estimated as 1150–1200° C., but probably lower.

Ore feed began at 6.40 P.M. All charged at 10.30 P.M. Finished 11.45 P.M.

Coal burned between 6 and 11 P.M. was 5,530 pounds, or 1,106 pounds per hour.

Coal burned per ton of raw ore was 0.245 ton, or 24.5 per cent., or 30.6 per cent. of the roasted ore.

Heat distribution better than in previous runs but temperature was not high enough in the upper kiln.

Sample.	Sulphur. Per cent.
16a 8.10 P.M. First ore through	0.63
17 8.30 P.M. Average of first part of ore roasted	0.72
18 8.45 P.M. Kiln hotter. Ore well nodulized	1.24
19 9.05 P.M. Kiln slightly cooler	1.25
20 9.40 P.M. Kiln heat more even. Flue temp. rising	1.20
21 9.45 P.M. 10 min. after giving more air through pulverizer	1.28
22 10.20 P.M. After cooling, just sintering again	1.15
23 10.30 P.M. Nodulizing well; more air	1.10
24 11.10 P.M. Feed cut off at 10.30. Large nodules	0.66
B-3 Average of all roasted ore	1.06

This run failed because upper part of kiln was not hot enough. It was an improvement on preceding runs. The sulphur removal was 75 per cent.

RUN NO. 4.—HIGH SULPHUR IRON ORE.

Nov. 26, 1910, 12.05 P.M.–4.45 P.M.

		Suphur.
	Per cent.	Per cent.
Size of screened ore {	on 3/4-inch screen	4.48
	on 1/2-inch screen	24.63
	through 1/2-inch screen	70.89
		4.49

Rate of feed, 2 tons per hour. About 11 tons fed.

Rate of kiln revolution, 2 minutes and 20 seconds, or 140 seconds.

Ore passes through kiln in 1 2/3 hours, or at 0.70 foot per minute.

Flue temperature:

12 M.	2 P.M.	2.15 P.M.	2.30 P.M.	2.50 P.M.	3.10 P.M.	4 P.M.	4.50 P.M.
900 to 1000° C.	700° C.	690° C.	735° C.	780° C.	800° C.	790° C.	800° C.

Kiln temperature, too cold.

Coal used was 2 tons or 18.2 per cent. of the ore.

Ore feed began at 12.05 P.M. Shut down with kiln full at 4.45 P.M.

Flue gas analyses:

	4.00 P.M.	4.50 P.M.
Carbon dioxide.....	17.00 per cent.	18.00 per cent.
Oxygen.....	6.5 per cent.	5.5 per cent.

Damper choked and air cut to minimum.

Sample No.	Sulphur. Per cent.
25 1.40 P.M. First ore. 1 1/2 hrs. in hot kiln. Flue 900–1000° C. at start	0.17
26 1.50 P.M. Furnace cooling, nodules smaller	0.44
27 2.00 P.M. Furnace cooling more, nodules 1 inch and smaller	0.63
28 2.10 P.M. Furnace cold, ore not fusing	2.26
29 2.30 to 3.05 P.M. Furnace warming up, small nodules	1.89
30 3.05 to 3.15 P.M. Insufficient heat in desulphurizing zone	1.94
31 3.15 to 3.30 P.M. Furnace cooling again	1.89
32 3.30 to 3.50 P.M. Not hot enough. Increased heat	2.16
33 4.35 P.M. Well nodulized, but too cold last hour	1.94
34 4.45 P.M. Temperature now seems about right	1.73
B-4 Average of run	1.84

Summary.—Sample No. 25 shows what could have been done if the temperature of 900 to 1000° C. had been kept up in the flue and upper part of the kiln with correspondingly higher temperature in the rest of the kiln. Limiting the air supply caused irregular and incomplete working.

EXPERIMENT 4-A.—ANALYSES OF KILN SAMPLES OF RAW AND ROASTED ORE AFTER RUN NO. 4.

Sample No.		Sulphur. Per cent.
35	Ore 2 ft. from discharge, dense nodules $\frac{1}{2}$ -1 inch	1.60
36	Ore 5 ft. from discharge, dense $\frac{1}{8}$ - $\frac{3}{8}$ -inch nodules	1.58
37	Ore 7 ft. from discharge, small nodules adhering	1.50
38	Ore 9 ft. from discharge, clinkered masses	1.47
39	Ore 11 ft. from discharge, dense, fused slag	1.69
40	Ore 13 ft. from discharge	1.77
41	Ore 15 ft. from discharge	2.12
42	Ore 17 ft. from discharge	2.04
43	Ore 19 ft. from discharge	2.36
44	Ore 21 ft. from discharge, angular pieces bonded by sintered fines	3.40
45	Ore 24 ft. from discharge, still black but not sintered	3.61
46	Ore 27 ft. from discharge. Ore loose. Color dark brown	4.13
47	Ore 30 ft. from discharge. Ore loose. Color light brown	4.30
48	Ore 33 ft. from discharge. Ore loose. Color lighter brown	4.06
49	Ore 36 ft. from discharge. Ore loose. Color about same	4.40
50	Ore 39 ft. from discharge. Ore loose. Color about same	3.97
51	Ore 42 ft. from discharge	4.15
52	Ore 47 ft. from discharge	3.95
53	Ore 52 ft. from discharge	3.94
54	Ore 57 ft. from discharge	3.74
55	Ore 62 ft. from discharge	4.04
56	Ore 67 ft. from discharge	4.35

Sulphur elimination apparently began at 24-27' from entrance. Irregularities before that were doubtless due to uneven composition of the ore and to concentration of sulphur due to the escape of carbon dioxide.

RUN NO. 5.—HIGH SULPHUR IRON ORE.

Nov. 28, 1910, 3.30 to 10.00 P.M.

Rate of kiln rotation, once in 4 minutes.

This run was made with screened and crushed ore like that used for runs Nos. 3 and 4. Several accidents occurred involving four shut-downs (40 minutes, 30 minutes, 5 minutes and 18 minutes). At no time was the kiln hot enough. The quality of the coal was thought to be at fault. Analyses showed the "Hocking" slack, which was used, contained 4 per cent. more ash and 2 per cent. less volatile matter than the Pennsylvania No. 8 slack, afterwards used. Flue temperatures, 900-680° C.

It is doubtful whether this was the only cause of the failure of this run.

The first ore which came through the kiln was partly roasted and was the best produced in the whole run.

Sample No.		Sulphur. Per cent.	Iron. Per cent.
8 P.M.	57	Fairly well roasted ore.	1.31 49.2

FLUE GAS ANALYSES.

	Carbon dioxide. Per cent.	Oxygen. Per cent.
Maximum.....	18.4	10.0
Minimum.....	13.0	4.60

RUN NO. 6.—HIGH SULPHUR IRON ORE.
Nov. 29, 1910, 10.40 A.M.—6.00 P.M.

	Moisture. Per cent.	Sulphur. Per cent.
Size of ore		
on 3/4-inch screen	4.41	
on 1/2-inch screen	27.80	2.7 4.29
through 1/2-inch screen	67.79	

Rate of feed, 2 to 2 $\frac{1}{2}$ tons per hour. Ore used, approximately 15 tons.

Coal used was 4.4 tons or 29.3 per cent.

Rate of kiln rotation, one turn in four minutes.

Ore passed through kiln in 2 $\frac{1}{2}$ hours, or at 0.47 foot per minute.

Flue temperatures:

10.40 A.M.	10.55 A.M.	11.30 A.M.	12.30 P.M.	12.50 P.M.	1.25 P.M.	2.15 P.M.	5 P.M.
960° C.	920° C.	880° C.	880° C.	850° C.	875° C.	860° C.	Hotter.

Sample No.		Sulphur. Per cent.
58	1.30-1.40 P.M. Represents effect of hot kiln 2 $\frac{1}{2}$ hrs. before	0.40
59	2.00-2.15 P.M. Well nodulized. Kiln cooler	0.66
60	2.35-2.45 P.M. Well nodulized. Kiln cooler	0.80
61	3.00-3.15 P.M. Increased coal. Still making large nodules	0.80
62	3.30-3.45 P.M. Snowballing nicely. (Making large porous nodules)	0.82
63	4.00-4.15 P.M. No ring noticeable	0.71
64	4.30-4.45 P.M.	0.78
65	5.00-5.15 P.M. Kiln a trifle hotter	0.72
66	5.30-5.45 P.M. Shut down with kiln full at 6 P.M.	0.64

FLUE GAS ANALYSES.

	1 P.M. Per cent.	1.20 P.M. Per cent.	1.45 P.M. Per cent.	4.00 P.M. Per cent.	5.45 P.M. Per cent.
Carbon dioxide.....	17	15	13	16	16
Oxygen.....	6	8	10	7	7
				Sulphur. Per cent.	

Sample B-6, average of all roasted ore, run No. 6.....	0.85
Sample No. 67, largest pieces from run No. 6 (3 inches diam.).....	0.97

Our notes show that the kiln was heated more uniformly and to a higher average temperature than in any previous run. The flame was long and oxidizing. We attribute the improved results to the better heating. Sample No. 58 representing 960° C. flue temperature was the best.

EXPERIMENT NO. 6-A.—ANALYSES OF KILN SAMPLES OF RAW AND ROASTED ORE AFTER RUN NO. 6.

Sample No.		Sulphur. Per cent.
68	2 ft. in kiln. Nodulized	0.96
69	5 ft. in kiln. Nodulized	0.85
70	9 ft. in kiln.	0.90
71	13 ft. in kiln. Ring 11'-15'	1.42
72	17 ft. in kiln. Scoured. Agglomerated	1.60
73	19 ft. in kiln. Odor of sulphur dioxide	1.87
74	23 ft. in kiln. Slightly agglomerated by fine ore	2.83
75	27 ft. in kiln. Nearly black, very slightly agglomerated	3.83
76	31 ft. in kiln. Dark brown color	3.79
77	36 ft. in kiln. Medium brown color	3.82
78	41 ft. in kiln. Cinnamon-brown color	3.68
79	46 ft. in kiln. Cinnamon-brown color	3.64
80	51 ft. in kiln. Fox-brown color	3.66
81	56 ft. in kiln.	3.78
82	61 ft. in kiln. Gray-brown color	4.05
83	66 ft. in kiln. Gray-brown color	4.34

Comparing these analyses with those from No. 4-A, we see that the heated zone was hotter and extended farther up the kiln. Rapid desulphurization begins at 27 feet in run No. 6 and only at 21 feet in run No. 4.

RUN NO. 7.—HIGH SULPHUR IRON ORE.

Nov. 30, 1910, 1.35 P.M. to 10.20 P.M.

The ore used for this run was prepared by screening and crushing to pass $\frac{1}{2}$ inch and so was finer than any ore previously used.

Rate of feed was the same, 2 to 2 $\frac{1}{2}$ tons per hour.

Rate of kiln rotation, once in four minutes.

Ore passed through the kiln in approximately 2 $\frac{1}{2}$ hours.

Flue temperatures:

P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.	P.M.
1.35	2.35	2.55	3.20	4.20	5.10	6.00	7.00 7.15
815° C.	800° C.	795° C.	780° C.	800° C.	800° C.	800° C.	800° C. 820° C.

Coal used, 11,200 pounds equals 37.9 per cent.

Ore used was 12 tons (approximately). Ore feed was 1.37 tons per hour.

Sample No.		Sulphur. Per cent.
84	3.45-4.00 P.M. First ore through; part of No. 6.	1.10
85	4.45-5.00 P.M. Forming snowballs. New ore	0.83
86	5.15-5.30 P.M.	1.16
87	5.45-6.00 P.M.	1.02
88	6.15-6.30 P.M.	1.22
89	6.45-7.00 Small nodules. Kiln rather cool	1.36
90	7.15-7.30 P.M. Represents ore best heated	1.25
91-100	Taken while kiln was discharging; were not analyzed by us	
B-7	Average of run	1.18

This run was planned in order to show the effect of fine ore. The temperature was not high enough, nor the heated zone extended enough to desulphurize either coarse or fine ore. Fine ore travels more slowly in the kiln and makes more flue dust.

FLUE GAS ANALYSES.

	Carbon dioxide. Per cent.	Oxygen. Per cent.
Maximum.....	16.2	8.4
Minimum.....	14.6	7.0

RUN NO. 8.—HIGH SULPHUR IRON ORE.

Dec. 1, 1910, 9.00 A.M. to 6.00 P.M.

The ore size was larger for this than for any previous runs except Nos. 1 and 2. It was *screened to pass 1 1/2 inch* and not further crushed.

Rate of kiln rotation, once in 245 seconds.

Rate of feed approximately 1 1/2 tons per hour. 25 tons roasted.

Sulphur in raw ore used was 4.30 per cent.

Coal used was 4 tons or 16 per cent. (approximately).

Draft, 0.1 inch by water gauge. Best heat distribution so far.

Stack damper open wide.

Flue temperatures:

A.M.	A.M.	A.M.	A.M.	A.M.	P.M.	P.M.	P.M.
9.00	9.15	9.30	9.45	10.20	12.06	1.06	4.00
1000° C.	1000° C.	965° C.	950° C.	950° C.	960° C.	980° C.	980° C.

Flue temperature constant between 1.00 P.M. and 4.00 P.M.

FLUE GAS ANALYSES. (No material variation.)

Sample No.	Carbon dioxide. 15.0 per cent.	Oxygen. 2.0 per cent.	Sulphur. Per cent.
101	12.45-1.00 P.M. First ore through		0.036
102	1.15-1.30 P.M. Small nodules. Some fall to dust		0.030
103	1.45-2.00 P.M. Like small grapes. Kiln hotter		0.086
104	2.15-2.30 P.M. Hot zone far up kiln		0.133
105	2.45-3.00 P.M. Nodules about 1 inch		0.086
106	3.15-3.30 P.M. Larger nodules. Nearly all dust		0.074
107	3.45-4.00 P.M. Very porous pieces		0.065
108	4.15-4.30 P.M.		0.040
109	4.45-5.00 P.M.		0.026
110	5.15-5.20 P.M.		0.021
111	5.45-6.00 P.M.		0.019
B-8	Average of all roasted ore		0.047

It is evident from this run that with the temperature in flue above 950° C. and not over 1000° C. complete desulphurization is continuously possible. We believe that speed of feed and size of ore could be increased.

EXPERIMENT NO. 8 A.—ANALYSIS OF RAW AND ROASTED ORE IN KILN AFTER RUN NO. 8.

Sample No.		Sulphur.
112	Ore 2 ft. from discharge	Trace
113	Ore 5 ft. from discharge	Trace
114	Ore 9 ft. from discharge	Trace
115	Ore 13 ft. from discharge	Trace
116	Ore 16 ft. from discharge	Trace
117	Ore 18 ft. from discharge	0.041 per cent.
118	Ore 20 ft. from discharge	0.036 per cent.
119	Ore 22 ft. from discharge	0.034 per cent.
120	Ore 24 ft. from discharge	0.110 per cent.
121	Ore 26 ft. from discharge	0.240 per cent.
122	Ore 31 ft. from discharge	0.66 per cent.
122a	Ore 31 ft. from discharge. Lumps above average size	0.61 per cent.
123	Ore 36 ft. from discharge	1.12 per cent.
124	Ore 38 ft. from discharge.	1.36 per cent.
124a	Ore 38 ft. from discharge. Lumps above average size	0.80 per cent.
125	Ore 40 ft. from discharge	1.49 per cent.
126	Ore 42 ft. from discharge	1.70 per cent.
127	Ore 44 ft. from discharge	1.90 per cent.
127a	Ore 44 ft. from discharge. Lumps 2 inches X 3 inches X 1 inch.	1.86 per cent.
128	Ore 46 ft. from discharge	2.37 per cent.
129	Ore 48 ft. from discharge	2.56 per cent.
130	Ore 50 ft. from discharge	3.06 per cent.
131	Ore 52 ft. from discharge	3.85 per cent.
132	Ore 54 ft. from discharge	4.01 per cent.
133	Ore 57 ft. from discharge	3.90 per cent.
134	Ore 60 ft. from discharge	3.97 per cent.
135	Ore 65 ft. from discharge	3.57 per cent.

LENGTH OF DESULPHURIZING ZONE.

It is noteworthy that in this experiment the ore began to be desulphurized rapidly after traveling only 18 feet in the kiln.

In run No. 6, the ore traveled 53 feet and in run No. 4, 49 feet before the sulphur began to be rapidly eliminated.

The first half of the sulphur is eliminated in the next eight feet in run No. 8. The next fourth of the sulphur is expelled in the next eight feet. The sulphur is practically all expelled during 30 feet of travel in a kiln estimated to be at 1100-1200° C., the flue gases actually escaping at 980° C.

RATE OF TRAVEL THROUGH DESULPHURIZING ZONE.

The ore moved through this hot zone at the rate of 70 feet in 150 minutes, or 30 feet in 64 minutes, equivalent to 0.47 foot per minute. In other words, the sulphur in 1 1/2-inch ore is reduced under these conditions in 28 feet to below 0.25 per cent., and in 30 feet below 0.1 per cent., and the time required closely approximates one hour.

These facts have a very direct bearing on design of kiln for roasting this ore.

LOSS OF WEIGHT OF ORE WHEN ROASTED IN A ROTARY KILN.

This is more clearly shown by the increase in iron percentage than by the weights of roasted ore recovered. The following figures are calculated from the iron percentages. The losses in weight thus found correspond very closely to the losses on ignition when the powdered samples of raw ore are ignited in a covered crucible. This fact indicates to us that practically all the iron is in the unoxidized condition in the roasted ore. There must be an oxidation of

some of the iron during sulphur expulsion, but reduction follows when the union with silica, lime, magnesia and manganese takes place.

Sample.		Loss in	
		Iron.	kiln roast.
		Per cent.	Per cent.
A-10	Raw ore used for run No. 4.....	41.57	19.22
B-4	Average roasted ore, run No. 4.....	51.46
A-12	Raw ore used for run No. 6.....	41.17	21.97
B-6	Average roasted ore, run No. 6.....	52.62
A-14	Raw ore used for run No. 8.....	41.26	21.21
B-8	Average roasted ore, run No. 8.....	52.37
		Loss on ignition (covered crucible).	
Sample of "Cargo" taken when unloaded..		40.66	19.86

ANALYSIS OF RAW AND ROASTED ORE.

	Cargo sample.	Run No. 8 (raw).	Run No. 8 (roasted).
Iron.....	40.66 per cent.	41.26 per cent.	52.37 per cent.
Manganese.....	1.95 per cent.	n. d.	2.58 per cent.
Sulphur.....	4.01 per cent.	4.30 per cent.	0.047 per cent.
Phosphorus.....	n. d.	n. d.	0.012 per cent.
Silica.....	6.32 per cent.	n. d.	9.05 per cent.
Lime.....	7.40 per cent.	n. d.	8.48 per cent.
Magnesia.....	5.10 per cent.	n. d.	4.81 per cent.
Carbon dioxide....	21.80 per cent. (calc.)	21.21 per cent. (roast loss)	n. d.

The loss on ignition in an open crucible is the difference between oxygen absorbed and volatile matters expelled. In a covered porcelain crucible we found nearly all of the CO₂ and 2/3 of the sulphur expelled.

LABORATORY "LOSS ON IGNITION" TESTS SHOWING THE STRONG AFFINITY OF THE ROASTED BUT UNSINTERED ORE FOR OXYGEN.

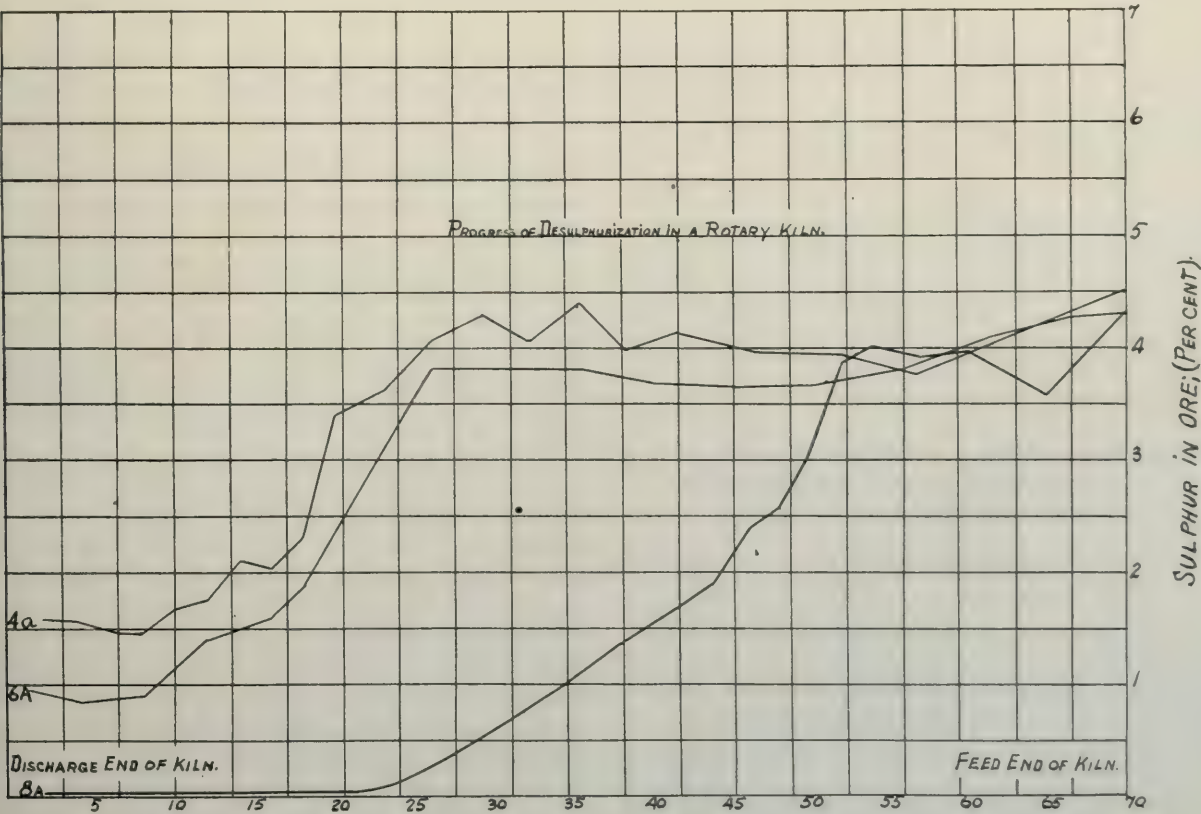
		Loss on ignition	
Sample No.		Porcelain crucible (covered).	Platinum crucible (open).
		Per cent.	Per cent.
46	27 ft. in kiln after run No. 4.....	2.86 loss	3.44 gain
47	30 ft. in kiln after run No. 4.....	3.66 loss	2.26 gain
48	33 ft. in kiln after run No. 4.....	5.68 loss	0.84 gain
49	36 ft. in kiln after run No. 4.....	6.66 loss	0.48 loss
50	39 ft. in kiln after run No. 4.....	7.86 loss	2.72 loss
51	42 ft. in kiln after run No. 4.....	10.56 loss	5.80 loss
52	47 ft. in kiln after run No. 4.....	11.66 loss	7.44 loss
53	52 ft. in kiln after run No. 4.....	17.42 loss	9.98 loss
54	57 ft. in kiln after run No. 4.....	18.24 loss	11.72 loss
55	62 ft. in kiln after run No. 4.....	...	11.86 loss
56	66 ft. in kiln after run No. 4.....	18.26 loss	...

RELATION OF FLUE TEMPERATURE TO ROASTING EFFICIENCY.

It was observed that the first ore through the rotary kiln was always the best. Usually the initial temperature of the kiln was considerably higher than the average of the run.

We believe that these tests in the earlier runs show how vital it was to maintain a temperature in the kiln high enough to give 950 to 1000° C. in the flue, as was the case in the successful run No. 8.

Average test of run.				
Run No.	Initial temperature, Degrees C.	Sulphur in first ore, Per cent.	Temperature, Degrees C.	Sulphur, Per cent.
2	910	0.95	733	1.70
3	815	0.72	772	1.06
4	950 (approx.)	0.17	756	1.81
6	960	0.40	877	0.85
7	815	0.83	800	1.21
8	1000	0.036	970	0.047



EFFECT OF RATE OF HEATING THE ORE.

Run No. 8, in which the kiln was heated to 1000–1100° C. nearly to the point where the ore entered, left us in some doubt whether the more open structure of the roasted ore was not produced by the sudden heating. It was thought that the complete sulphur elimination might have been made possible by the porosity thus produced.

We compared the rate and completeness of sulphur removal from ore placed in a hot kiln at 1000 and 1100° C. with that from ore placed in the kiln when firing up. We found that the elimination of sulphur was most complete in the latter case, thus disproving the idea that sudden heating is necessary.

Undoubtedly the rapid passage of hot gases causes the carbon dioxide elimination in the rotary kiln to be very quickly accomplished. The sulphur elimination is initiated earlier and carried more evenly to completion.

PROGRESS OF DESULPHURIZATION IN A ROTARY KILN.

By examining the curves plotted by us under the above title it will be observed that the rapid elimination of sulphur did not begin until the carbon dioxide had been practically all removed.

In runs Nos. 4 and 6, on account of the low temperatures, 70 per cent. of the kiln length was used in expelling carbon dioxide.

In run No. 8 only 25 per cent., or 17½ feet, was thus used. This was due to the higher and more even temperature.

LENGTH OF KILN.

The length of kiln which seems to be indicated for roasting this ore is one which will give a zone 30 feet long at 1100–1200° C. preceded by one 20 feet long at 900–1100° C. There should be also a warming up section of sufficient length to utilize the heat of the fuel.

We do not think that a kiln less than 125 feet will meet requirements.

CONCLUSION.

The authors desire to state that the rotary kiln test was participated in by several other engineers and chemists and that every one concerned should share in the credit for results accomplished. It is understood that the publication at this time of names of persons and places is not permitted.

PITTSBURGH TESTING LABORATORY, PITTSBURGH.

**SPECIFICATIONS FOR THE PURCHASE OF FUEL OIL FOR
THE GOVERNMENT, WITH DIRECTIONS FOR
SAMPLING OIL AND NATURAL GAS.¹**

By IRVING C. ALLEN.

Received September 20, 1911.

GENERAL STATEMENT.

Until within a few years fuels were generally bought solely on the statement of the seller. The consumer made little effort to find whether value was received for the price paid, but relied on the integrity of the dealer and the brand or trade name of the fuel.

Recently, however, the plan of purchasing coal

according to specifications of quality, especially heating value, has gained favor. This plan has been adopted by various bureaus of the Government and by many private corporations, and the total quantity of coal bought under such specifications now amounts to millions of tons yearly. The specifications in use differ in detail, but those that are most precise provide for payment on the basis of the heating value and the ash, moisture, and sulphur content of the fuel as delivered.

In consequence of the success that has attended the use of heating-value specifications in buying and selling coal there has arisen a demand for similar specifications, based on careful tests, to govern the purchase of fuel oils and the refined products of petroleum. These specifications, to be satisfactory, should establish not only the heating value of the oil, and thus show, like the specifications for coal, the number of heat units the purchaser obtains for a given price per unit quantity of fuel, but also the physical character of the oil, its flash point and burning point, and the quantity of extraneous matter it contains.

It is evident that an essential feature of any such plan of purchasing oil in bulk is an equitable method of sampling deliveries—that is, a method that insures the taking of representative samples.

The Bureau of Mines has received many inquiries from Government bureaus and from private concerns regarding fuel-oil specifications and the sampling of purchases. In reply to these inquiries the bureau issues this paper, which, although intended primarily for the guidance of Government officials, may be of service, the bureau trusts, to all persons who buy or sell fuel oil.

GENERAL SPECIFICATIONS.

(1) In determining the award of a contract, consideration will be given to the quality of the fuel offered by the bidders, as well as the price, and should it appear to be to the best interest of the Government to award a contract at a higher price than that named in the lowest bid or bids received, the contract will be so awarded.

(2) Fuel oil should be either a natural homogeneous oil or a homogeneous residue from a natural oil; if the latter, all constituents having a low flash point should have been removed by distillation; it should not be composed of a light oil and a heavy residue mixed in such proportions as to give the density desired.

(3) It should not have been distilled at a temperature high enough to burn it, nor at a temperature so high that flecks of carbonaceous matter began to separate.

(4) It should not flash below 60° C. (140° F.) in a closed Abel-Pensky or Pensky-Martens tester.

(5) Its specific gravity should range from 0.85 to 0.96 at 15° C. (59° F.); the oil should be rejected if its specific gravity is above 0.97 at that temperature.

(6) It should be mobile, free from solid or semi-solid bodies, and should flow readily, at ordinary atmospheric temperatures and under a head of 1 foot of oil, through a 4-inch pipe 10 feet in length.

¹ Published by permission of Director Bureau of Mines, Washington, D. C.

(7) It should not congeal nor become too sluggish to flow at 0° C. (32° F.).

(8) It should have a calorific value of not less than 10,000 calories per gram¹ (18,000 British thermal units per pound), 10,250 calories to be the standard. A bonus is to be paid or a penalty deducted according to the method stated under Section 21, as the fuel oil delivered is above or below this standard.²

(9) It should be rejected if it contains more than 2 per cent. water.

(10) It should be rejected if it contains more than 1 per cent. sulphur.

(11) It should not contain more than a trace of sand, clay, or dirt.

(12) Each bidder must submit an accurate statement regarding the fuel oil he proposes to furnish. This statement should show:

(a) The commercial name of the oil.

(b) The name or designation of the field from which the oil is obtained.

(c) Whether the oil is a crude oil, a refinery residue, or a distillate.

(d) The name and location of the refinery, if the oil has been refined at all.

(13) The fuel oil is to be delivered f. o. b. cars or vessel, according to the manner of shipment, at such places, at such times, and in such quantities as may be required, during the fiscal year ending

(14) Should the contractor, for any reason, fail to comply with a written order to make delivery, the Government is to be at liberty to buy oil in the open market and charge against the contractor any excess of price, above the contract price, of the fuel oil so purchased.

SAMPLING.

(15) Deliveries of fuel oil will be sampled by a representative of the Government. Whenever such action is practicable, the oil will be sampled as it is being delivered. The final sample will be made from samples taken from as large a proportion of the delivery as practicable, in order that the final sample may truly represent the delivery.

(16) The final sample will be sealed and forwarded to the Federal Bureau of Mines, Pittsburg, Pa., for analysis.

(17) If the contractor so desires, permission will be given him, or his representative, to witness the sampling of the delivery and the preparation of the final sample.

(18) The final sample will be analyzed and tested immediately after its receipt in Pittsburg.

CAUSES FOR REJECTION.

(19) A contract entered into under the terms of these specifications shall not be binding if, as the re-

¹ Calories $\times 1.8$ = British thermal units per pound.

² It is important that the standard fixed should not be higher than can be maintained under the terms of the contract. In the absence of information as to the heating value of the oil, the Bureau of Mines will analyze samples taken from the deliveries to establish the standard heating value, expressed in calories or British thermal units. It will be to the best interests of the contractor to specify a fair standard for the fuel oil he offers, since failure to maintain that standard will cause deduction from the contract price and possibly the cancellation of the contract, while deliveries of higher quality than the standard will result in the contractor receiving premiums.

sult of a practical service test of reasonable duration, the fuel oil fails to give satisfactory results.

(20) It is understood that the fuel oil delivered during the terms of the contract shall be of the quality specified. The frequent or continued failure of the contractor to deliver oil of the specified quality will be considered sufficient cause for the cancellation of the contract.

PRICE AND PAYMENT.

(21) Payment for deliveries will be made on the basis of the price named in the proposal for the fuel oil corrected for variations in heating value,¹ as shown by analysis, above or below the standard fixed by the contractor. This correction is a *pro rata* one and the price is to be determined by the following formulae:

$$\frac{\text{Delivered calories per gram (or B. t. u. per lb.)} \times \text{contract price}}{\text{Standard calories per gram (or B. t. u. per lb.)}} = \text{price to be paid.}$$

Water that accumulates in the receiving tank will be drawn off and measured periodically. Proper deduction will be made by subtracting the weight of the water from the weight of the oil deliveries.

DETERMINATION OF WEIGHT FROM VOLUME.

The specifications given on the preceding pages provide for the purchase of fuel oil by weight. As such oil is frequently delivered by volume, it is important to note the temperature of a delivery and to allow for the expansion due to this temperature when computing the weight of the delivery from the volume. From the volume of the oil at the temperature of delivery, the volume at standard temperature (15° C.) should be computed in the manner given below.

The coefficient of expansion of ordinary fuel oil residues of asphaltic base is approximately 0.0006 per 1° C.

Hence if the temperature (N° C.) of the delivery is above 15° C., then (N° C. — 15° C.) \times 0.0006 = correction.

This correction is to be added to the specific gravity at N° C. to give the standard specific gravity, that at 15° C.

If the temperature (N° C.) of the oil delivered is below 15° C., the correction ((15° C. — N° C.) \times 0.0006) is to be subtracted from the specific gravity at 15° C.

Since a gallon of water at a temperature of 15° C. weighs 8.3316 pounds, the weight in pounds of a gallon of oil at 15° C. is 8.3316 times the specific gravity of the oil at that temperature.

Similarly, since a cubic foot of water at 15° C. weighs 62.3425 pounds, the weight in pounds of a cubic foot of oil at 15° C. is 62.3425 times its specific gravity at that temperature.

REPORTING ANALYSES OF FUEL OIL.

The following form is used by the Bureau of Mines in

¹ The value of an oil as fuel is in proportion to the total combustible matter it contains as shown by its heating value. This value may be expressed in small calories per gram of B. t. u. per pound. Sulphur, moisture, and earthy matter lower the heating value of an oil and decrease the furnace capacity; they also may have a deleterious effect on boiler and furnace, and may impair the operation of burners.

reporting the results of an analysis of a sample of fuel oil:

DEPARTMENT OF THE INTERIOR.

BUREAU OF MINES.

WASHINGTON, D. C., 191-.

SIR:

In reference to the sample of fuel petro-
(Quantity.)
leum representing of petroleum delivered at
(Quantity.)
a temperature of ...° C. by the as
(Company delivering.)
a product, from the
(Crude, residue, or distillate.) (Lease.)
....., to
(Field or district.) (County.) (State.)
the at on
(Department receiving.) (City.)
....., I have the honor to report as fol-
(Date of delivery.)

lows:

Specific gravity at 15° C.
(Baumé at 59° F.)
Calorie per gram
(B. t. u. per pound)
Water, per cent.
Sulphur, per cent.
Earthy matter, sand, etc., per cent.
Flash point, ° C. (Abel-Pensky, or Pensky-
Martens, closed tester)
Burning point, ° C. (same tester, opened) ..
Remarks:

.....
.....
The above information is for the use of the Government and the dealer or operator furnishing the oil. It is to be considered confidential until it is published by the United States Government.

Respectfully,

.....
Chief Clerk.

Certified:

.....
Petroleum Chemist.

SAMPLING PETROLEUM OR FUEL OIL.

GENERAL STATEMENT.

The accuracy of the sampling and, in turn, the value of the analysis must necessarily depend on the integrity, alertness, and ability of the person who does the sampling. No matter how honest the sampler may be, if he lacks alertness and sampling ability, he may easily make errors that will vitiate all subsequent work and render the results of tests and analyses utterly misleading. A sampler must be always on the alert for sand, water, and foreign matter. He should note any circumstances that appear suspicious, and should submit a critical report on them, together with samples of the questioned oil.

SAMPLING WAGON DELIVERIES.

SAMPLING WITH A DIPPER.

Immediately after the oil begins to flow from the wagon to the receiving tank, a small dipper holding any definite quantity, say 0.5 liter (about 1 pint),

is filled from the stream of oil. Similar samples are taken at equal intervals of time from the beginning to the end of the flow—a dozen or more dipperfuls in all. These samples are poured into a clean drum and well shaken. If the oil is heavy, the dipperfuls of oil may be poured into a clean pail and thoroughly stirred. For a complete analysis the final sample should contain at least 4 liters (about 1 gallon). This sample should be poured into a clean can, soldered tight and forwarded to the laboratory.

It is important that the dipper be filled with oil at uniform intervals of time and that the dipper be always filled to the same level. The total quantity of oil taken should represent a definite quantity of oil delivered and the relation of the sample to the delivery should be always stated, for instance: "1 gallon sample representing 1 wagon-load of 20 barrels."

CONTINUOUS SAMPLING.

Instead of taking samples with a dipper, it may be more convenient to take a continuous sample. This may be taken by allowing the oil to flow at a constant and uninterrupted rate from a 1/2-inch cock on the under side of the delivery pipe during the entire time of discharge. The continuous sample should be thoroughly mixed in a clean drum or pail, and at least 4 liters (about 1 gallon) of it forwarded for analysis. A careful examination should be made for water, and if the first dipperful shows water this dipperful should be thrown into the receiving tank and not mixed with the sample for analysis.

MIXED SAMPLES.

If the oil delivered during any definite period of time, say one month, be from the same source and of uniform quality (but only in case it is of uniform quality), it may suffice to pour definite proportional quantities of the dipper and the continuous samples taken during this period into a tinned can or drum having a tight screw cap or bung. An iron drum should not be used, since even a clean iron surface will absorb sulphur by long contact with a sulphur-containing oil, and this sulphur will be lost to the analyst. At the end of the month a number of round, clean stones should be put into the drum and the drum should be rolled to insure intimate mixing. Then 4 liters (about 1 gallon) of the gross sample should be taken for analysis. The drum should be drained, rinsed clean with gasoline, dried, and made ready for a second sampling.

The all-important point is that the gross sample, whatever the manner of sampling, shall be made up of equivalent portions of oil taken at regular intervals of time, so that the sample finally forwarded for analysis will truly represent the entire shipment.

SAMPLING A LARGE TANK OR RESERVOIR.

Water or earthy matter settles on standing. Hence, before a large stationary tank or reservoir is sampled the character of the contents at the bottom should be ascertained by dredging with a long-handled dipper, and the content of the dipper should be examined critically. If a considerable quantity of sedi-

ment is brought up, it should be cause for rejecting the oil.

The sampling of a large stationary tank or reservoir of oil, particularly if the oil has stood so long that it has begun to stratify, or form layers of different density, may be done as follows:

The sampler should procure an ordinary iron pipe, or preferably a tinned tube, 1 inch in diameter and long enough to reach from above the manhole, where he can grasp it, to the bottom of the tank. The lower end of the pipe should be reamed out with a round file. A conical plug of cork, wood, or other suitable material should be fitted to this end, and a strong, stiff wire, such as the ordinary telegraph wire, run through this plug and up through the pipe to a point where it can be grasped firmly by the sampler. A pull on the wire will close the bottom of the pipe, and a rap against the bottom of the tank will drive the plug home and make an oil-tight seal or valve.

To operate this sampling device, the sampler should remove the plug, allow it to drop some three inches below the bottom of the pipe, and let it hang there by the wire extending above the pipe. Then holding the pipe, open at top and bottom, in a vertical position, the sampler should allow it to sink slowly through the oil to the bottom of the tank. He should do this slowly and with care, so that the pipe will penetrate the oil without agitating it and will thus cut a representative core of oil from the surface to the bottom. When the pipe touches the bottom, the sampler should draw up the slack of the wire and pull the plug into place; then he should strike the plug smart against the bottom of the tank, thereby driving it home and sealing the pipe. He can then withdraw the pipe and pour the oil into the sampling can. If it seems desirable, he should "core" or "sample" a reservoir at regularly spaced points, unite these samples, mix them thoroughly, and take 4 liters (about 1 gallon) of the gross sample for analysis.

Instead of a pipe sampler, a bottle holding half a liter (about 1 pint) may be used. It should be securely fastened to a long pole and have a loosely-fitted stopper tied to a strong cord. The bottle, corked and empty, is immersed to any desired point within the mass of oil, and the stopper is pulled out. The bottleful of oil is poured into a suitable receiving vessel, and the bottle, thoroughly drained, is made ready for a second filling. Bottlefuls of oil taken in this way from points symmetrically placed throughout the mass of oil, will, if properly mixed, provide an excellent gross sample from which to take the 4-liter (1 gallon) sample for analysis.

SAMPLING A SINGLE DRUM.

A single drum may be sampled with a glass tube. This tube, open at both ends, should be grasped at the top, held vertically, inserted in the drum without agitating the oil, and allowed to cut its way slowly to the bottom of the drum. The upper end should then be closed with the thumb or forefinger of the hand holding it, the tube withdrawn, and the oil on the outside wiped off with the fingers of the other

hand. The sample in the tube can then be transferred to a small can, and forwarded for analysis.

FORWARDING SAMPLES.

The sample should be forwarded in a glass bottle or carboy or in a tin can, preferably in the latter because less liable to breakage. If a tin can is used the cap should be soldered tight. The can should not be filled completely; about an eighth of an inch of space should be left to allow for possible expansion of the oil.

The can should be sealed as soon as it is filled to avoid loss by volatilization of the lighter constituents of the sample. After the can has been filled and tightly soldered, it should be wiped clean and carefully examined for pinholes or small leaks. All leaks should be soldered before the can is packed for shipment.

The bottle or can should be carefully labeled. The following form of label,¹ used by the Bureau of Mines, should be placed on samples shipped to the bureau:

DEPARTMENT OF THE INTERIOR.

BUREAU OF MINES.

Information to Accompany Each Sample of Fuel Petroleum Submitted for Analysis.

Sample number.....	Sampled by.....
Oil delivered to.....	(Department receiving.)
Place of delivery.....	(City.) (State.)
Quantity of oil delivered.....	
Date of delivery.....	
Temperature of oil as delivered° C.....	
Name of contractor.....	
Nature of oil.....	(Crude, residue, or distillate.)
If refined to any degree, state name and location of refinery.....	
Source of oil.....	(Lease.) (Field or district.) (County.) (State.)
Remarks.....	
Date of forwarding sample.....	
Forwarded by..... via.....	(Express or fast freight.) (Transportation line.)

Date of receipt of sample by Bureau of Mines.....
 Condition of sample when received by Bureau of Mines.....

The label should be carefully written with a hard lead pencil on a strong mailing tag, and this tag should be securely tied to the can. The lead pencil should be pressed firmly against the tag so as to indent its surface. An inscription thus written is legible even after the paper has been wet with oil. Gummed labels should not be used; they are easily detached if slightly moistened, and may be lost. A

¹ These labels will be furnished on request.

duplicate copy of the record on the label should be mailed to the engineer in charge, Bureau of Mines, Pittsburgh, Pa.

SAMPLING GAS FROM A WELL.

Since the gas associated with oil is an ideal fuel and illuminant, and the literature dealing with the composition of natural gas is scanty, a description of the method of sampling such gas for analysis is here given.

For taking a sample of gas under pressure from an oil well a cloth funnel should be made by folding and sewing any strong, closely woven cloth into the form of a cornucopia. The larger end of this funnel should be large enough to encompass the gas pipe from which the sample is to be taken. The smaller end, or apex, of the funnel should be securely tied about one end of a flexible rubber tube 1 or 2 feet long and one-fourth to one-half inch in diameter. If there is a gas jet at the well, one end of the rubber tube may be attached directly to the jet.

A gas-sampling bottle should be procured, if practicable, from the Bureau of Mines, Pittsburgh, Pa. If such a bottle is not at hand, a 1- or 2-liter (1- or 2-quart) bottle with a well-ground, tight-fitting glass stopper may be used. The bottle should be thoroughly cleansed and dried. A large perfume bottle or an acid bottle, such as may be obtained from a drug store, will usually answer. A glass stopper is essential, for a cork or rubber stopper may leak, even though it appears to be hermetically sealed with wax; moreover, a cork or rubber stopper may contaminate the gas.

To collect a sample, the funnel should be tied firmly about the end of the gas pipe. The funnel and the rubber tube should then be thoroughly flushed with the gas to rid them of air. The free end of the tube should go to the bottom of the sample bottle. The bottle should be fastened bottom up and the gas allowed to blow strongly into it for at least a quarter of an hour to insure complete expulsion of air. If the gas pressure is low, the gas should be allowed to blow longer, or until it is certain that all air has been expelled from the bottle. Meanwhile the stopper of the bottle should have been well greased with vaseline.

While the gas is still blowing through the tube the tube should be slowly withdrawn. The stopper should be put in just as soon as the tube is withdrawn and should be turned firmly into place. Then the bottle should be turned up and a spoonful of melted paraffin poured over the stopper. The stopper should be secured with elastic band.

A strong tag should be tied to the bottle by a stout cord. This tag should be labeled as follows:

Gas Sample.

Sampled by.....
 Date.....
 Well..... Lease.....
 (Number.)
 Section.....Township.....Range.....
 District.....County.....State.....
 Remarks.....

The bottle should be packed securely in a box and forwarded to the Bureau of Mines, Pittsburgh, Pa. A duplicate copy of the label should be sent to the same address.

BUREAU OF MINES, DEPT. OF INTERIOR.

THE DETERMINATION OF TOTAL SULPHUR IN INDIA RUBBER.¹

By C. E. WATERS AND J. B. TUTTLE.

Received August 7, 1911.

What may still be described as the usual method for the determination of total sulphur in India rubber is the one first published by Henriques.² The details of this method are too well known to require description here. In more recent years other methods have been advocated. Alexander³ used sodium peroxide to decompose the nitrogen peroxide addition-product of rubber. In the same year, Esch⁴ recommended the use of Eschka's mixture and procedure for the determination of sulphur in coal. He also stated that the sodium peroxide method gives good results.

Wagner⁵ published a slight modification of the method of Henriques, stating that much sulphur is lost by volatilization. He therefore made the nitric acid solution alkaline with sodium hydroxide, transferred to a nickel crucible, added sodium carbonate and then evaporated to dryness. The oxidation was carried to completion by heating in an air-bath.

Pontio⁶ fused with manganese peroxide and a mixture of sodium and potassium carbonates. The results were about 0.1 per cent. lower than by the method of Henriques. For the free sulphur⁷ he extracted with absolute alcohol, distilled off the solvent, oxidized with alkaline hydrogen peroxide, evaporated to dryness and fused in a silver crucible.

A distinct departure from the usual methods is due to Hinrichsen⁸ who oxidizes electrolytically in the presence of concentrated or fuming nitric acid.

Finally, Hübener⁹ devised a method intended to exclude insoluble mineral sulphates. The sample is boiled in a flask with concentrated nitric acid for some time, most of the acid evaporated off on the steam-bath and the oxidation completed by means of bromine and water.

One of the present writers, having frequent occasion to determine total sulphur in rubber, over a year ago made a number of comparative tests of different variations of the method of Henriques. The results obtained with two samples of rubber are given below (I-IV). In all cases 0.50 gram of rubber was taken. All fusions were made over a flame of gasoline-air gas. The results are given as percentages of sulphur. All reagents were tested, and no determinations have been omitted.

I. Warmed 2½ hours in covered crucible with 25 cc. concentrated HNO₃, allowed to stand 36 hours,

¹ Published by permission of the Director of the Bureau of Standards.

² *Z. angew. Chem.*, **12**, 902 (1899).

³ *Gummi-Ztg.*, **18**, 729; *Z. angew. Chem.*, **17**, 1799 (1904).

⁴ *Chem.-Ztg.*, **28**, 200 (1904).

⁵ *Gummi-Ztg.*, **21**, 552; *C. A.*, **1**, 1327 (1907).

⁶ *Caoutchouc et Gutta-Percha*, **6**, 2751; *Chem. Techn. Rep.*, **1909**, 372.

⁷ *Ibid.*, **5**, 2194; *C. A.*, **3**, 3412 (1908).

⁸ *Chem.-Ztg.*, **33**, 735 (1909).

⁹ *Gummi-Ztg.*, **24**, 213-4; *Analyst*, **35**, 266-7 (1910).

evaporated nearly to dryness, added $\text{Na}_2\text{CO}_3\text{-KNO}_3$ mixture and fused as usual.

Sample	1	1	2	2
Sulphur.....	3.39	3.44	3.26	3.22

II. Added HNO_3 and one cc. Br, let stand 36 hours without preliminary heating, evaporated, etc., as usual.

Sample	1	1	2	2
Sulphur.....	3.40	3.47	3.39	3.27

III. The same as II, but allowed to stand only one hour, heated with cover for two hours, evaporated and fused as usual.

Sample	1	1	2	2
Sulphur.....	3.31	3.35	3.04	3.09

IV. Only HNO_3 added, digested at once on the steam-bath for two hours, evaporated and fused.

Sample	1	1	2	2
Sulphur.....	3.17	3.43	3.06	2.93

V. Treated with one cc. Br and five cc. H_2O , allowed to stand over night without heating, next morning evaporated off the H_2O , added HNO_3 , digested, evaporated and fused.

Sample	1	1	2	2
Sulphur.....	3.71	3.65	3.37	3.38

In an attempt to obtain satisfactory results without fusion, some determinations were made some months later, without a knowledge of Hübener's paper. Half-gram portions of a sample of medium hard rubber were digested with nitric acid in flasks covered with watch-glasses. In some cases bromine was added after the digestion with acid and, after standing half an hour, water was added and the flasks heated on the steam-bath. Finally, the volume was brought to about 175 cc., the solution heated, filtered and a little sodium hydroxide added to the filtrate and wash-water. This was then evaporated to dryness, adding a little hydrochloric acid towards the end, taken up with very dilute hydrochloric acid, filtered, and barium sulphate precipitated as usual. The results follow:

VI. Treated with HNO_3 alone.

Sulphur.....	7.76	7.51	7.68	7.96
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VII. Treated with HNO_3 , followed by Br.

Sulphur.....	7.62	7.51	7.93	7.87	7.76
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All of the precipitates obtained under VI and VII contained much lead.

After the method of Hübener was called to our attention, some determinations were made on a sample of hard rubber containing no barium.

VIII. Hübener's method.

Sulphur.....	4.79	3.91	5.23	4.02	4.31	4.13
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It is evident that very widely different amounts of sulphur must have been retained in the insoluble residue in the form of lead sulphate.

IX. Total sulphur by method of Henriques.

Sulphur.....	8.65	8.70
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X. Treated with HNO_3 , followed by Br and H_2O and fused as usual.

Sulphur.....	8.63	8.62	8.77	8.80	8.72	8.80
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It has recently been claimed by van't Kruijs¹ that

¹Z. anal. Chem., 49, 393 (1910).

when an excess of calcium chloride over the amount of sulphuric acid is present, only calcium sulphate is carried down with the barium sulphate, and the calcium salt can be converted into barium sulphate by digestion with strong hydrochloric acid, or *aqua regia*, and barium chloride. Several determinations were made to test this suggestion.

XI. Preliminary treatment as under X, subsequent treatment as suggested by van't Kruijs.

Sulphur.....	8.73	8.76	8.52	8.46	8.74	8.78	8.75	8.77
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At this point joint analyses of a fairly large sample of rubber were carried out by the present writers.

XII. Hübener's method. The sulphur in the insoluble residue was determined by fusion with soda-salt-peter mixture, extracting the melt with water, etc., as usual.

S in original filtrate....	0.91	0.91	0.68	0.79	0.82	0.99	1.52	1.15	1.24
S in insoluble residue....	2.35	2.43	2.54	2.69	2.53	2.36	1.95	2.31	2.21

Total sulphur found....	3.26	3.34	3.22	3.48	3.35	3.35	3.47	3.46	3.45
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All of the precipitates of barium sulphate from the original filtrates were found to contain lead, when tested with dilute ammonium sulphide.

XIII. Treated with HNO_3 , allowed to stand over night, the acid driven off on the steam-bath, one cc. Br and ten cc. H_2O added; then the H_2O and excess of Br driven off by heating. The residue was mixed with soda and salt-peter and fused as usual.

Sulphur.....	3.41	3.21
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XIV. The same as XIII, but the HNO_3 not driven off before adding Br.

Sulphur.....	3.60	3.63	3.58	3.63	3.57
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XV. The same as XIII, but treatment with Br omitted.

Sulphur.....	3.29	3.49	3.35	3.38	3.55	3.43	3.36	3.58	3.56
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XVI. Treated first with Br and H_2O , allowed to stand over night without heating, then Br and H_2O driven off on steam-bath, treated with HNO_3 , etc., and fused.

Sulphur.....	3.45	3.47	3.48	3.53	3.49
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XVII. The same as XVI, but excess Br and H_2O not driven off before adding HNO_3 .

Sulphur.....	3.59	3.47	3.64
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XVIII. The method of Henriques, except that the HNO_3 was saturated with Br.

Sulphur.....	3.66	3.65	3.62	3.73	3.68	3.65	3.69	3.63	3.66	3.71	3.62
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XIX. The same as XVIII, but followed by the treatment suggested by van't Kruijs.

Sulphur.....	3.69	3.73	3.76	3.75
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In order to obtain a definite idea of the variations caused by differences in the preliminary treatment and in the conditions under which the barium sulphate is precipitated, a very dilute solution of sulphuric acid was made. In each of the following determinations, a 25-cc. portion was taken. The weights of barium sulphate found were calculated as percentages of sulphur in 0.50 gram of rubber in order that the results might be more readily compared with the determinations above.

XX. Direct precipitation with BaCl_2 . The last

two determinations were made with the addition of two cc. of 1 : 1 HCl, the first six without adding HCl.

Sulphur..... 3.11 3.11 3.11 3.11 3.11 3.11 3.10 3.11

XXI. Evaporated off the water from 25 cc. of the dilute H_2SO_4 , added the soda-salt peter mixture and fused as usual.

Sulphur..... 3.12 3.15 3.12

XXII. Like XXI, but added CaCl_2 to the solution of the melt before precipitating BaSO_4 and treated the latter according to van't Kruijs.

Sulphur..... 3.22 3.18 3.19

XXIII. Like XXII, but did not digest the precipitated BaSO_4 , nor evaporate the filtrate to recover traces of dissolved BaSO_4 .

Sulphur..... 3.13 3.12 3.11

XXIV. Like XXI, but did not fuse. The solution was acidified with HCl.

Sulphur..... 3.17 3.19 3.16

XXV. Added 250 cc. H_2O and ten cc. concentrated HCl to twenty-five cc. dilute H_2SO_4 , added BaCl_2 , digested two hours, poured off the supernatant liquid, digested the BaSO_4 with one cc. ten per cent. BaCl_2 and fifteen cc. HCl (1 : 1). Diluted, filtered, evaporated the combined filtrates to dryness in platinum, took up with fifty cc. of slightly acidified H_2O and collected the slight residue on the same filter.

Sulphur..... 3.12 3.10 3.11

XXVI. Exactly neutralized NaOH solution with the dilute H_2SO_4 , using phenolphthalein as indicator. After each addition of acid the solution was heated, in a platinum dish, until the pink color no longer reappeared; then evaporated to dryness, ignited gently and weighed as Na_2SO_4 .

H_2SO_4 used (cc.).....	75.56	75.55
Na_2SO_4 found (gm.).....	0.2082	0.2080
BaSO_4 equivalent to Na_2SO_4 (gm.).....	0.34197	0.34164
BaSO_4 equivalent to 25 cc. H_2SO_4 (gm.).....	0.1131	0.1130
Sulphur (calc. on 0.5 gm. rubber).....	3.11	3.11

XXVII. The same as XXVI, but used NaHCO_3 instead of NaOH.

H_2SO_4 used (cc.).....	45.01	43.48
Na_2SO_4 found (gm.).....	0.1240	0.1194
BaSO_4 equivalent to Na_2SO_4 (gm.).....	0.20367	0.19612
BaSO_4 equivalent to 25 cc. H_2SO_4 (gm.).....	0.1131	0.1128
Sulphur (calc. on 0.5 gm. rubber).....	3.11	3.10

In order to test the completeness of the oxidation of sulphur by means of the nitric acid-bromine mixture, the following determinations were carried out.

XXVIII. Powdered sulphur crystals, digested in the cold with twenty cc. HNO_3 and an excess of Br. Finally added twenty cc. H_2O and heated on the steam-bath for about two hours. Then evaporated nearly to dryness, took up with water and precipitated with BaCl_2 .

Sulphur taken (gm.).....	0.0483	0.0395	0.0561
Sulphur found (gm.).....	0.0481	0.0399	0.0563

XXIX. Powdered sulphur crystals treated at the same time as some of the samples of rubber. The exact methods are referred to in the table, the Roman numerals indicating the method employed.

Method	I.	II.	III.	IV.	V.
Sulphur taken (gm.)....	0.0528	0.0619	0.0494	0.0646	0.0411
Sulphur found (gm.)....	0.0485	0.0590	0.0479	0.0595	0.0414
Sulphur (per cent.)....	91.84	95.33	96.91	92.13	100.67

In the determinations by methods I to IV, part of the sulphur was not attacked by the nitric acid nor by the sodium carbonate added before making the fusion. Part, at least, of this unattacked sulphur was seen to burn when the fusion was made.

As stated above (XII), the barium sulphate precipitates representing soluble sulphates, etc., in the Hübener method, were found to contain lead. Lead sulphate dissolves slightly and is, besides, partially decomposed by water, hydrobromic and nitric acids, etc.¹ In order to get an idea of the amount of barium sulphate to be expected to result from the decomposition and solution of lead sulphate under the conditions of Hübener's method, some determinations were made. Lead sulphate was first prepared by precipitation from a hot, dilute, nitric acid solution of lead nitrate by means of a hot, dilute solution of sulphuric acid. It settled rapidly as a coarse-grained powder, which was washed by decantation with hot water, then in a Gooch crucible with hot water, followed by strong alcohol. It was then dried in an air-bath.

In the first experiments it was treated with hot water and the amount of barium sulphate precipitated from the filtrate was calculated as percentage of sulphur in 0.50 gram rubber.

XXX. Washed 0.200-gram portions of PbSO_4 on filters. Each time 250 cc. hot water were used. The filtrates were slightly acidified with HCl and precipitated with BaCl_2 .

Sulphur..... 0.24 0.25

These precipitates contained only traces of lead.

XXXI. Treated 0.200-gram portions of PbSO_4 , according to Hübener's method, slightly modified. Treated with thirteen cc. concentrated HNO_3 , evaporated practically to dryness on the steam-bath, added fifty cc. H_2O , 0.5 cc. Br and two cc. of dilute HNO_3 (1 : 4). Heated, filtered, and washed with about 200 cc. hot water. Then precipitated with BaCl_2 .

Sulphur..... 0.73 0.80 0.57

These precipitates contained a little lead.

From these determinations it seems quite certain that the larger part of the sulphur found as soluble sulphate under XII must have come from the solution and decomposition of lead sulphate first formed when the rubber was attacked by nitric acid.

At the suggestion of Dr. Hillebrand, four determinations were made of the amount of lead carried down with the barium sulphate precipitated in the usual way from the aqueous extract of the fusion mass. In spite of the presence of a large excess of sodium carbonate some lead goes into solution. The preliminary treatment was according to XVIII, and two grams of rubber, instead of 0.50 gram, were taken each time.

XXXII. After fusion the melts were dissolved in water. To each of the first two there was added two grams of sodium bicarbonate in order to decompose any alkali plumbate. The solutions were heated on the steam-bath for one and one-half hours and then filtered from the insoluble. After acidifying with

¹ Kolb, *Dingl. poly. J.*, **209**, 268; Ditte, *Ann. chim. phys.*, [5] **14**, 190.

hydrochloric acid, barium sulphate was precipitated as usual.

	1.	2.	3.	4.
BaSO ₄ found (gm.).....	0.5379	0.5395	0.5437	0.5417
Sulphur (per cent.).....	3.69	3.71	3.73	3.72

The barium sulphate precipitates were then mixed with soda and potash and fused. The melts were dissolved in water, filtered and the residues washed with hot, very dilute sodium carbonate solution. The residues of barium carbonate and lead oxide were then dissolved in dilute nitric acid and the lead precipitated from the cold solutions by hydrogen sulphide. After standing over night in stoppered flasks, the precipitates of lead sulphide were filtered off washed, dissolved in nitric acid and finally converted into sulphate by evaporating down in porcelain crucibles with sulphuric acid and gently igniting.

	1.	2.	3.	4.
PbSO ₄ found (gm.).....	0.0086	0.0071	0.0040	0.0045
Equivalent to BaSO ₄ (gm.).....	0.0066	0.0055	0.0031	0.0035
Corrected BaSO ₄ (gm.).....	0.5359	0.5379	0.5428	0.5407
Corrected sulphur (per cent.)....	3.68	3.69	3.73	3.71

It is quite evident from these figures that although notable quantities of lead sulphate are carried down with the barium sulphate, the correction in the percentage of sulphur is negligible.

The filtrates from the original precipitates were treated with hydrogen sulphide and gave slight precipitates. The alkaline filtrates from the barium carbonate and lead oxide were tested with ammonium sulphide and became brown. The next day there was a slight film of a dark color on the bottom of each of the beakers in which these solutions were tested. This was probably a mixture of small amounts of lead and iron sulphides. In all the solutions tested, as well as in the actual determinations of lead sulphate, greater amounts of lead were found in 1 and 2, which had been treated with bicarbonate. Apparently at the temperature of the steam-bath the lead bicarbonate probably formed was not decomposed.

CONCLUSIONS.

Treatment of the rubber with nitric acid alone gives low results (compare XV with XVIII). This is probably largely due to loss of free sulphur, since nitric acid alone does not completely oxidize sulphur to sulphuric acid in the length of time ordinarily taken for a determination.

The Hübener method cannot be employed in the presence of mineral fillers which tend to form insoluble sulphates. This applies especially to barium carbonate and litharge.

A comparison of XX to XXVII shows that the fusion method gives results very close to those obtained by direct precipitation and by neutralization. The van't Kruys method gives high results.

The best results seem to be obtained by the use of method XVIII, according to which the rubber is decomposed by means of nitric acid saturated with bromine.

CONSISTENCY OF PAINTS BY THE STORMER VISCOSIMETER.

By ALLEN PUGH AND A. H. SABIN

Received June 9, 1911.

Those who have ever attempted to take the viscosity of a paint will appreciate that it is no easy matter. At a meeting in Atlantic City, last June, it was suggested by Mr. P. H. Walker and Prof. A. H. Sabin that the Stormer viscosimeter might be used for this purpose, especially the apparatus, as modified, at the suggestion of Mr. C. N. Forrest, from the paddle to the cylinder type.

It was the writers' desire to obtain some method for checking the exact consistency of a large number of paints, and do it in such a manner that the personal factor would be eliminated. A sample of paint was, therefore, prepared which, in the writers' judgment, was of the proper consistency for application. The viscosimeter was adjusted with this paint so that the dial made a complete revolution in two minutes. A sample of paint made by the Patton Paint Co. came very close to the paint made by the writer, as well as one made by the Sherwin-Williams Co. To get a more definite standard, however, 95 per cent. glycerine was tested and, strange to relate, the dial made a complete revolution in exactly two minutes. Therefore, glycerine, at 20°C., was taken as the standard, and all subsequent tests made at this temperature.

During the past two months several hundred viscosities have been taken, and although the machine has been tested each morning before the day's work it has not been found necessary to readjust the weights. The apparatus, however, requires quite a bit of attention and should be frequently cleaned and oiled. It is very essential also to have the temperature exact, as one degree will make quite a difference in the reading.

The viscosimeter consists of a flat-bottomed cylindrical cup $1\frac{7}{8}$ inches internal diameter by $2\frac{1}{2}$ inches deep having two radial vertical wings or septa $\frac{1}{4}$ inch wide attached to its inner wall, and extending from the bottom to within $\frac{5}{8}$ inch of the top, being in fact obstructions to the rotary flow of the liquid. Within this cup is suspended a stirrer, the revolution of which is resisted by the viscosity of the liquid; this stirrer is a hollow metal cylinder $1\frac{3}{8}$ inches long and $1\frac{1}{4}$ inches in diameter, its lower end open, the upper end closed except it contains four holes, each $\frac{3}{16}$ inch in diameter, symmetrically arranged. This cylinder is supported from above by a vertical rod or shaft, concentric with the cylinder but external to it, being $\frac{3}{16}$ inch in diameter by $2\frac{1}{4}$ inches long. The end of this is attached by a collar and screw to the bottom of a vertical shaft which carries a pinion $\frac{1}{2}$ inch in diameter, having 25 teeth, which in turn is driven by a gear $5\frac{1}{4}$ inches in diameter with 275 teeth, to which large gear is attached a drum $1\frac{1}{2}$ inches in diameter, around which is wound a small silk cord, the external portion of which passes over a small pulley and is attached to a driving weight. The top of the shaft carrying the small gear carries also a screw or worm which engages and drives the

serrated edge of a graduated disk or dial, one revolution of which marks 100 revolutions of the stirrer. The stirrer is suspended so that its bottom is $\frac{3}{8}$ inch above the bottom of the cup, and in consequence its top is $\frac{3}{4}$ inch below the top of the same; when in use the cup is filled to within $\frac{3}{8}$ inch of its top with liquid which, therefore, stands $\frac{3}{8}$ inch above the top of the stirrer. To make a hundred revolutions of the stirrer the weight descends about 39 inches. The stirrer comes within $\frac{1}{16}$ inch of each side of the radial wings, one on each side of the cup, already mentioned.

The index of viscosity may be defined as the force required to produce a given shear in a given time; if we adopt a minute as the unit of time, and the shear produced by 100 revolutions of the stirrer as the unit shear, the viscosity will be indicated by the number of grams (units of weight) required to cause the stirrer to revolve 100 times in one minute. Allowance should be made for the friction of the machine, which in this instrument is about 5 grams.

It has a friction clutch which, being opened, allows it to start; it is used with a stop-watch. As at present sold it is not provided with a suitable scale-pan and weights, but is supposed to be used with a fixed weight, which is sufficient if we wish only to bring various mixtures to one standard, but is like using a fixed measure instead of a scale. It is very important to use it at a standard temperature.

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A STUDY OF CARBON IN SEWAGE AND SEWAGE PURIFICATION.

By H. W. CLARK AND GEORGE O. ADAMS.¹

Received June, 1 1911.

The part that nitrogen plays in sewage and sewage purification and in the analysis of sewage and water is well known to all engaged in sanitary work that has to do with water and sewage or their purification. The important part played by carbon and carbonaceous matter is, however, not so well understood; neither is the relation that carbon bears to nitrogen in the composition of sewage and water, in analytical work and in sewage purification, fully comprehended. Carbon, however, is the chief constituent of the organic matter in sewage and is a troublesome factor in the satisfactory disposal of sewage. It is carbonaceous matter, moreover, that gives color and other objectionable characteristics to some water supplies. To such sanitary chemists and engineers as construct, operate or study sewage plants, sewage filters, etc., the problem of carbon disposal appears more and more important. This is especially true when industrial sewage is to be treated. For a more complete understanding of that portion of the problem of sewage purification that has to do with carbon, studies have been made at the Lawrence Experiment Station from time to time during the past ten years in regard to the amount of carbon in sewage and water; the relation that carbon in samples undergoing analysis bears to the results of loss on ignition and oxygen

consumed determinations and to other bodies that may be determined by the analysis of sewage and water, and of the work accomplished by various classes of sewage filters in caring for the purely carbonaceous bodies in the sewage applied to them. In various reports of the Experiment Station during the past seven or eight years, much data accumulated in these studies have been given. In this work as elaborated in the reports, many comparisons have been made between the amount of nitrogen and carbon in the samples analyzed and the relative amount of oxygen necessary to oxidize the carbon compounds as compared with the amount necessary to oxidize the nitrogenous bodies in sewage.

The following paper presenting a summary of much of this carbon work, together with the results of additional studies, can be properly divided into several sections. Between some of these sections there may not seem to be any very clearly defined relation, but all have to do with carbon, nitrogen and oxygen in sewage and its purification.

(1) No. 1 deals with the determinations of the actual amount of carbon in samples of sewage and water and gives a comparison of the amount of this carbon with the amount of organic and other matter determined by the loss on ignition process; (2) No. 2 is in regard to relative amounts of carbon and nitrogen in sewage; (3) No. 3 deals with the relation between carbon and fatty matters in sewages; (4) No. 4 compares the per cent. that carbon forms of the loss on ignition determinations when sands from sewage filters that have been in operation are examined; (5) No. 5 gives the results of a series of studies of the oxygen consumed process, so-called, and what it shows in regard to carbonaceous and nitrogenous matter in water and sewage; (6) No. 6 treats of the relation between the amount of each oxidized or stored in such filters; and (7) No. 7 treats of the influence of carbon on nitrification.

CHAPTER NO. I.—COMPARISON OF CARBON AND LOSS ON IGNITION.

In order to determine and show the amount of carbon in average samples of sewage and water and the relation between carbon and loss on ignition, dry residues from the evaporation of forty-four samples of sewages, waters, etc., were obtained. These samples were as follows: Twelve samples of sewage and ten of the same samples after filtration through paper, nine samples of surface waters, three of well waters, five effluents from sand filters which had received sewage for many years, three effluents from trickling sewage filters operating at a high rate and two mill wastes, both unfiltered and filtered through paper. In obtaining these dry residues for analysis, the following precautions were taken: First, dust was carefully excluded during evaporation; second, the alkalinity of each sample was neutralized to avoid error in the final results due to the decomposition of carbonates during the combustion for the determinations of carbon, and an allowance was made for the decrease in weight of the residue due to neutralizing the carbonates. Carbon combustions were made by

¹ Lawrence Experiment Station, Mass. State Board of Health.

the usual method and to prevent the red fumes of nitrogen oxide evolved from being absorbed in the potash bulbs, a Geissler bulb filled with strong sulphuric acid was placed between the calcium chloride tubes and the potash bulb, and all but a slight trace of the nitrogen oxide thus absorbed, this precaution being necessary only with the residues of samples high in nitrates. The analyses of the sewage residues showed that carbon formed as an average 23 per cent. of the total residues and 50 per cent. of the total loss on ignition when loss on ignition was determined in the usual way.

Of the residue from the evaporation of surface waters, 7.5 per cent. proved to be carbon and, as an average, 26 per cent. of the total loss on ignition was carbon. Of the residues from the evaporation of the effluents from the sewage filters of coarse material, previously mentioned, 10 per cent. was carbon, and the average amount that the carbon in these residues was of loss on ignition was 36 per cent. It is of course true that most, if not all, of the organic compounds likely to be found in sewage have percentages of carbon varying nearly within these limits. Carbohydrates contain from 40 to 44 per cent. of carbon, albuminous bodies from 50 to 55 per cent. and such fats as we have separated from sewage, 62 per cent. Studying these averages it is seen that while "loss on ignition" is undoubtedly, as is generally believed, a fair measure of the organic matter present in samples of sewage and water, yet it does not, of course, bear a very constant relation to the per cent. of carbon present.

It might, perhaps, be mentioned here that if the samples undergoing ignition contain nitrates, the loss of nitrogen during ignition, due to the reduction of these nitrates, is considerable. To illustrate this, nine residues of effluents from sewage filters ignited in the usual way in a platinum radiator, lost on an average 1.23 parts of nitric nitrogen for each part of "oxygen consumed" shown by the sample. If each part of nitric nitrogen is equivalent to 4.3 parts N_2O_5 , this loss is considerable when nitrates and oxygen consumed are both high, as is often the case in the effluents from sewage filters of coarse materials.

TABLE SHOWING THE AMOUNTS OF CARBON IN WATERS, SEWAGES, ETC.

Sample.	Carbon. Parts per 100,000.	Per cent. carbon in residue on evapora- tion.	Per cent. carbon in volatile matter. (Loss on ignition.)
Average of 12 samples of sewage:			
Unfiltered.....	19.7	22.8	50
Filtered.....	6.6	12.5	39
Average of 3 samples from contact and trickling filters:			
Unfiltered.....	7.0	9.9	36 ¹
Filtered.....	2.6	5.1	22 ¹
Average of 5 samples from sand sewage filters.....	1.47	4.5	18 ¹
Average of 9 samples of surface waters....	0.39	7.5	26
Average of 3 samples of ground waters....	0.33	2.2	16 ¹
Wool scourings, unfiltered.....	98.3	17.2	54
Wool scourings, filtered.....	45.4	11.3	54
Paper mill waste, unfiltered.....	136.2	23.2	61
Paper mill waste, filtered.....	8.5	7.3	32

¹ Low, due to loss of nitrates during ignition.

COMPARISON OF NITROGEN AND CARBON.

The following table presents a comparison of the relative amount of nitrogen and carbon in the samples already discussed. It will be noticed that in the sewages the carbon averages more than five and one-half times the organic nitrogen and three and one-half times the total nitrogen. The other figures are equally interesting, especially those of the two mill wastes presented; namely, wool-scouring and paper mill wastes, for in these the carbon was respectively twenty-one and fourteen and one-half times the organic nitrogen. It will be noticed also that the carbon present in the samples of surface and ground waters was from sixteen to twenty times as great as the nitrogen present.

TABLE SHOWING RELATION BETWEEN CARBON AND NITROGEN IN WATERS, SEWAGES, ETC.

Sample.	Parts carbon.	Parts Kjeldahl nitrogen.	Parts total nitrogen.	Ratio of Kjeldahl nitrogen to C/N.	Ratio of total N to carbon C/N.
Average of 12 samples of sewage:					
Unfiltered.....	19.7	1.68	5.64	11.7	3.5
Filtered.....	6.6	0.70	4.71	9.4	1.4
Average of 3 samples from contact and trickling filters:					
Unfiltered.....	7.0	1.06	5.37	6.6	1.3
Filtered.....	2.6	0.35	3.16	7.3	0.81
Average of 5 samples from sand sewage filters.....	1.47	0.19	2.58	7.7	0.57
Average of 9 samples of surface waters.....	0.39	0.025	0.048	15.8	8.1
Average of 3 samples of ground waters.....	0.33	0.016	0.120	20.5	2.7
Wool scourings, unfiltered....	98.3	4.57	5.81	21.1	16.9
Wool scourings, filtered.....	45.4	2.29	3.46	19.8	13.2
Paper mill waste, unfiltered...	136.2	9.31	10.30	14.6	13.2
Paper mill waste, filtered.....	8.5	0.55	0.65	15.5	13.1

CARBON, LOSS ON IGNITION AND FATS.

In determining the organic matter in sludges and sediments high in organic matter, the probable errors due to chemically combined water, mentioned on subsequent pages, are relatively small because the organic matter may be a hundred or more times greater than any loss of chemically combined water, while with the sands, figures in regard to which are given later, the organic matter is frequently much less than the amount of chemically combined water. Results of analyses for the determination of carbon and organic matter determined by "loss on ignition" of sludges and sediments are shown in a following table. The table shows that one-half of the organic matter in certain sewage sludges is fatty matter; and it will be seen that the carbon present in the sludge of fresh sewage is approximately 55 per cent. of the loss on ignition, and in trickling filter or contact filter sediments, 50 per cent. of the loss on ignition. In septic sewage sludge, the percentage of carbon is apparently a little higher, varying from 56 per cent. to 61 per cent. About 35 per cent. of the total carbon is represented by the carbon of the fats present in fresh sewage, while in septic sewage the carbon of the fats is about 25 per cent. of the total carbon.

TABLE SHOWING AMOUNTS AND COMPOSITION OF ORGANIC MATTER IN SEWAGE SLUDGES AND IN SEDIMENTS FROM FILTERS OF COARSE MATERIAL.

Sample.	Per cent. loss on ignition.	Per cent. carbon.	Per cent. Kjeldahl nitrogen.	Per cent. fats.
Average of 4 fresh Lawrence sewage sludges.....	66.9	37.3	24.9
Average of 12 Andover sewage sludges.....	48.4	27.1	1.49	19.9
Average of 4 septic tank sludges	49.1	28.8	11.3
Average of 9 sediments from sewage filters of coarse material.....	42.9	21.3	1.78

TABLE SHOWING RELATIONS BETWEEN CONSTITUENTS OF SLUDGES IN PRECEDING TABLE.

Sample.	Per cent. carbon is of loss on ignition.	Per cent. fats are of loss on ignition.	Per cent. carbon in fats is of total carbon.	Ratio of carbon to Kjeldahl nitrogen.
Average of 4 fresh Lawrence sewage sludges.....	55.8	37.2	41.4
Average of 12 Andover sewage sludges.....	56.0	41.1	45.5	18.2
Average of 4 septic tank sludges	58.7	23.0	24.3
Average of 9 sediments from sewage filters of coarse material.....	49.7	4.2	5.2

CARBON AND LOSS ON IGNITION—SANDS.

In estimating the amount of organic matter present in sands by the loss on ignition of such sands, there is a large error due to the loss of chemically combined water during ignition. This loss may even be 1 per cent. of the total weight of the samples taken, when the sand is clean, although it is usually lower. In order to determine how much of the loss on ignition in clean sands is due to organic matter and how much to chemically combined water, combustions were made on two clean sands, and these results are given in the following table:

TABLE SHOWING RESULTS OF COMBUSTIONS OF TWO CLEAN SANDS.

Number.	Per cent. loss on ignition.	Per cent. carbon.	Per cent. H ₂ O recovered.
1.....	0.32	0.000	0.33
2.....	0.33	0.015	0.32

The table shows that the carbon results average about 35 per cent. of the loss on ignition results and the carbon found in these sands was from seven to twelve times as great as the organic nitrogen that was found. Analyses of other sands follow:

TABLE SHOWING RELATION BETWEEN CARBON, NITROGEN AND ORGANIC MATTER STORED IN SANDS.

Sample.	Loss on ignition. Per cent.	Carbon. Per cent.	Per cent. that carbon is of loss on ignition.	Per cent. of nitro- gen.	Ratio of carbon to Kjeldahl nitrogen.	Total nitrogen.
Filter No. 1 sand:						
Average 3 inches	2.16	0.947	43.8	0.08	11.55
Average 9 inches	1.75	0.648	37.0	0.10	6.29
Average 12 inches	1.15	0.362	31.5	0.05	7.18
Filter No. 6 sand:						
Average 3 inches	3.26	1.091	33.5	0.12	8.78
Average 6 inches	3.14	1.083	34.5	0.11	10.00
Average 9 inches	3.07	1.183	38.5	0.10	11.80
Filter No. 9 sand:						
Average 3 inches	2.56	0.992	38.8	0.08	11.50
Average 6 inches	2.84	0.987	36.4	0.09	10.90
Average 9 inches	2.16	0.521	24.1	0.07	7.56
Regular sewage.....	10.40	3.30
Lawrence Street sewage.....	15.60	6.10
Septic sewage.....	7.10	1.10

OXYGEN CONSUMED.

It is well known that the "oxygen consumed" determination indicates only a portion of the organic carbon present in the water or sewage tested by this method and that that portion is not a constant; also that the "loss on ignition" determination includes some mineral as well as the organic matter present. The following figures show the percentage which the "oxygen consumed" obtained in the usual way (by five-minute acid-boiling) is of the oxygen actually required to oxidize the carbon in the following substances, these figures being determined by careful laboratory tests: With saccharose, 24 per cent.; dextrose, 22 per cent.; starch 0.17 per cent.; lactose, 9.6 per cent.; cellulose, 0.13 per cent.; and peptone, 5.7 per cent. Somewhat higher percentages are obtained when the process is applied to sewage, etc., this probably being due to the breaking down of complex bodies into simple and less stable compounds. On page 366 of the "Massachusetts State Board of Health Report for 1905," comparisons of two-minute, five-minute and thirty-minute boiling of samples with permanganate, or "oxygen consumed" results, are given. In this work oxygen consumed by both two- and five-minute boiling was determined on over six hundred samples of various kinds of water, sewage and effluents. The results by the two-minute method averaged for each class of water between 70 and 80 per cent. as high as the results by the five-minute method.

In further work, the "oxygen consumed" of thirty-six samples of sewage was determined by two-minute boiling and by heating in a boiling water bath for thirty minutes. As an average, the two-minute results were 55.5 per cent. of the thirty-minute results. In the samples in which carbon was determined, the heating with permanganate was continued until a maximum result was obtained. The samples were heated in free-flowing steam in an Arnold steam sterilizer. Usually eight hours were sufficient. Averaging all the samples, the results by the two-minute method were shown to be 33.8 per cent. of the maximum results.

From the known content of carbon in each sample, the oxygen required to oxidize it was calculated together with the per cent. which the "oxygen consumed" by the two-minute method and maximum methods were of this required carbon. In unfiltered sewages, the two-minute "oxygen consumed" was from 10 to 19, and the maximum "oxygen consumed" was from 34 to 54 per cent. of the oxygen actually required to oxidize the carbon. In the filtered sewages, higher percentages were obtained on account of absence of cellulose and these percentages were from 13 to 28 for the two-minute and for the maximum, from 51 to 86 per cent. of the oxygen actually required to oxidize the carbon. In the samples of effluents and waters, the percentages ran higher.

The following table presents some results of oxygen consumed tests upon the samples of sewage, water and wastes previously discussed in comparison with carbon and nitrogen.

TABLE SHOWING RELATION BETWEEN "OXYGEN CONSUMED" AND THE AMOUNT OF CARBON IN WATERS, SEWAGES, ETC.

Sample.	Parts oxygen consumed by prolonged acid boiling (max.).		Per cent. of carbon oxidized by prolonged acid boiling.	
	Parts oxygen consumed by 5-min. acid boiling.	Parts oxygen consumed by prolonged acid boiling (max.).	Per cent. of carbon oxidized by 5-min. acid boiling.	Per cent. of carbon oxidized by prolonged acid boiling.
Average of 12 samples of sewage:				
Unfiltered.....	8.09	25.6	15	49
Filtered.....	3.66	9.9	21	63
Average of 3 samples from contact and trickling filters:				
Unfiltered.....	3.69	9.2	22	80
Filtered.....	1.66	5.5	24	72
Average of 5 samples from sand sewage filters.....	1.03	1.61	25	49
Average of 9 samples of surface waters.....	0.40	0.63	38	64
Average of 3 samples of ground waters.....	0.17	0.71	17	53
Wool scourings, unfiltered....	49.00	235.00	19	90
Wool scourings, filtered.....	24.00	112.00	20	92
Paper mill waste, unfiltered....	70.80	247.00	20	68
Paper mill waste, filtered.....	4.80	21	..

CARBON AND NITROGEN APPLIED TO, AND STORED IN FILTERS.

The preceding tables show that the amount of carbon in sewage is from ten to fifteen times the organic nitrogen usually present. A considerable part of this carbon is present as cellulose and fats, of which the cellulose is especially stable, and it is these bodies which are chiefly responsible for the clogging of sewage filters. The following table shows the relation between the amounts of organic nitrogen and carbon applied to, stored in certain sewage filters, liberated or passing off in the effluents. A study of this table makes clear the very large amount of carbon applied as compared with organic nitrogen applied—about ten pounds of carbon to each pound of organic nitrogen. About seven times as much carbon as nitrogen is stored, as shown by the figures in the table.

TABLE SHOWING AMOUNTS OF ORGANIC NITROGEN AND CARBON STORED, APPEARING IN THE EFFLUENT AND OXIDIZED OR LIBERATED BY TRICKLING AND CONTACT FILTERS.

Period of operation (months).	Filter A. 72	Filter B. 72	Filter C. 31	Filter D. 23
Pounds per acre, applied:				
Kjeldahl nitrogen.....	226,200	210,700	45,800	65,900
Carbon.....	2,511,000	2,390,000	413,000	593,300
Pounds per acre, in effluent:				
Kjeldahl nitrogen.....	76,500	88,140	15,580	30,640
Carbon.....	566,100	652,200	90,400	226,800
Pounds per acre, stored:				
Kjeldahl nitrogen.....	10,390	12,600	16,500	18,670
Carbon.....	73,940	82,680	126,500	112,400
Per cent. in effluent:				
Kjeldahl nitrogen.....	33.8	41.8	34.0	51.7
Carbon.....	22.5	27.3	21.9	38.2
Per cent. stored:				
Kjeldahl nitrogen.....	4.6	6.0	36.0	31.5
Carbon.....	2.6	3.5	35.4	18.9
Per cent. oxidized and liberated:				
Kjeldahl nitrogen.....	61.6	52.2	30.0	16.8
Carbon.....	74.6	69.2	42.7	42.9

ORGANIC MATTER IN SAND FILTERS.

The discussion and analytical figures already given show very plainly that purely carbonaceous matter forms by far the larger portion of the organic matter

which we have to deal with in sewage and sewage purification. The percentage of nitrogen is small in the organic matter present in sewage and stored in filters. The reason that it has so prominent a place in all studies of water and sewage is that it is the chief constituent of matter that is easily changed, and its change from one form or combination to another shows clearly the transformation of a polluted liquid to a well purified liquid, and the analyses of the different combinations of nitrogen are necessary to show the composition of sewage and the purification taking place in filters, etc. The clogging which occurs in sand and other filters is mainly due, however, to carbon and fatty matters. If we take as a study three sand filters of fairly coarse sand which have been longest in operation at the Lawrence Experiment Station—at the present time this period of operation covering twenty-three years—we find by analysis of the sand of these filters that the stored nitrogen forms but about 4 or 5 per cent. of the total organic matters now retained by the sand, the remaining 96 per cent. being largely carbonaceous organic matter such as cellulose, fats, etc. The figures for stored matter in the three filters mentioned are as follows:

Filter No.	Stored nitrogen	Total organic matter stored during period of operation.
1	27 pounds	783 pounds
6	31 pounds	618 pounds
9A	29 pounds	590 pounds

Accurate determinations of the carbonaceous constituents of the organic matter stored in these three filters have been made by combustion furnace analyses, and the following tables give the amounts of carbon, and for purposes of comparison, determinations of organic matter by the loss on ignition method. As has been explained previously in this article, the loss on ignition gives figures that are high, and the total loss is not entirely organic matter, as is, of course, well known. The tables show that at least 75 per cent. of the stored carbonaceous matters are in the first foot in depth of each filter.

TABLE SHOWING AMOUNT OF CARBON, IN POUNDS PER ACRE PER FOOT OF SAND, IN FILTERS NOS. 1, 6 AND 9A.

Date.	Carbon in					Total	Per cent. of total which first foot yields
	First foot.	Second foot.	Third foot.	Fourth foot.	Fifth foot.		
	Filter No. 1.						
Oct. 1, 1907	43,080	5,930	2,710	2,400	2,450	56,570	76.2
	Filter No. 6.						
Oct. 1, 1907	58,280	10,520	5,590	3,900*	78,290	74.4
	Filter No. 9A.						
Oct. 1, 1907	50,800	4,380	3,260	3,540	1,290*	63,270	80.3
	TOTAL ORGANIC MATTER STORED, IN POUNDS PER ACRE PER FOOT OF SAND, IN LARGE FILTERS, AS DETERMINED BY LOSS ON IGNITION, CORRECTED FOR ORGANIC MATTER IN ORIGINAL SAND.						
	Filter No. 1						
July 1, 1908	104,520	21,800	11,100	5,800	13,340	156,560	66.7
	Filter No. 6.						
July 1, 1908	106,260	4,620	15,920	126,800	83.8
	Filter No. 9A.						
July 1, 1908	107,140	8,780	840	420	7,200	124,380	86.2

* Six inches only.

INFLUENCE OF CARBON UPON NITRIFICATION.

During the past fifteen years a large number of investigations have been made at the Station and elsewhere in the state in regard to methods for the disposal and purification of waste liquors from various industrial plants. During these studies certain results were obtained that caused us to believe that the activity of the nitrifying organism and the formation of nitrates were probably dependent upon the relation of carbon to nitrogen in the wastes studied. In order to determine whether or not this belief was true, a large number of special experiments are being made by us, and while not yet complete, the results so far obtained show that the carbon does have the influence that our observations seemed to show. A sewage or waste containing, say, x amount of nitrogen will, when submitted to oxidizing or nitrifying conditions in a filter, fail to nitrify if there is an amount of carbon equal to $10x$. Increasing the amount of nitrogen, however, will enable nitrification to take place, but this nitrification may again be checked by increasing the carbon. The results of the various investigations along this line will be presented in a subsequent paper.

STATE BOARD OF HEALTH, BOSTON.

COMPOSITION OF THE DRAINAGE WATER OF A SOIL WITH AND WITHOUT VEGETATION.

By LYTTLETON LYON AND JAMES A. BIZZELL.

Received July 20, 1911.

Drainage water was collected from twelve large tanks, a description of which has previously been published.¹ Each tank is slightly over four feet square and four feet deep with a capacity for about three and one-half tons of soil. They receive the natural rainfall but no other supply of moisture. Twelve tanks were filled with clay loam soil of uniform character in 1909 and crops were raised on certain of the tanks in 1910. The drainage water was meas-

and also the drainage between October 1, 1910, and May 1, 1911.

It is probable that the composition of the drainage water does not at present correspond exactly to that of the soil in the field. Monthly analyses of drainage from two of the plats show a gradual reduction in the concentration of the solution. The soil was well compacted when placed in the tanks, each horizontal foot being packed in the tanks in the relative position which it occupied in the field. As there has been almost no settling of the soil since these receptacles were filled, it is probable that no abnormal aeration is now taking place. The effect of plant growth during the summer of 1910 on the density and composition of the drainage water collected between Oct. 1, 1910, and May 1, 1911, is very apparent, when the flow from the unplanted tanks is compared with that from the tanks on which plants were raised. Owing to the fact that, of the drainage collected between May 23 and Oct. 1, a very small proportion was collected after the plants began to grow vigorously, this liquid does not show so markedly the effect of plant growth on the soluble matter of the soils.

Three tanks contained no plants, four were planted to maize and two to oats.

A statement of the average flow of drainage water by months from tanks unplanted, planted to maize and planted to oats is given in Table I. Both the maize and oat tanks were planted on May 23, the date on which the measurement of the flow of drainage began. Oats ripened about Aug. 7th and maize continued to grow until the latter part of September. The growth of the crops did not curtail the flow of drainage until July and even then the dry weather reduced the flow from the unplanted tanks practically as much as from the planted. The removal of water from the soil by the plant did not influence the flow of drainage until September and from then until

TABLE I.—FLOW OF DRAINAGE WATER (IN LITERS) FROM THE AVERAGE TANK WHEN UNPLANTED; WHEN PLANTED TO MAIZE AND WHEN PLANTED TO OATS

Tank Nos.	Crop.	May 23 to										Total from May 23, 1910, to May 1, 1911.	Total from Oct. 1, 1910, to May 1, 1911.
		June 1.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.
2, 4, 8	None	48.8	25.9	1.1	0.1	45.2	31.0	90.3	73.1	199.6	14.0	156.0	76.6
3, 5, 7, 9	Maize	44.6	24.3	0.8	0.0	0.6	0.1	0.0	4.8	176.9	9.0	172.6	84.5
6, 10	Oats	50.1	24.0	0.2	0.2	0.0	0.0	6.0	52.7	149.3	6.0	172.3	105.4
												566.2	491.7

TABLE II.—COMPOSITION OF DRAINAGE WATER, PARTS PER MILLION, MAY 23 TO OCT. 1, 1910

Tank Nos.	Crop.	Total solids.	Nitrates (NO ₃).	Bicarbonates (HCO ₃).	Silica (SiO ₂).	Phosphates (PO ₄).	Calcium (Ca).	Magnesium (Mg).	Potassium (K).	Sodium (Na).
2, 4, 8	None	606	73.7	372	8.9	trace	97.9	15.9	2.2	29.9
3, 5, 7, 9	Maize	389	31.9	286	7.7	trace	71.7	18.0	1.1	15.3
6, 10	Oats	430	45.6	255	9.6	trace	80.9	19.1	1.2	14.2

TABLE III.—COMPOSITION OF DRAINAGE WATER, PARTS PER MILLION, OCT. 1, 1910, TO MAY 1, 1911

Tank Nos.	Crop.	Total solids.	Nitrates (NO ₃).	Bicarbonates (HCO ₃).	Silica (SiO ₂).	Phosphates (PO ₄).	Calcium (Ca).	Magnesium (Mg).	Potassium (K).	Sodium (Na).
2, 4, 8	None	618	136.0	256.0	6.4	trace	96.8	18.7	2.6	25.8
3, 5, 7, 9	Maize	264	14.6	181.0	4.8	trace	52.9	8.4	2.2	21.1
6, 10	Oats	271	14.6	192.0	4.6	trace	52.1	8.8	4.0	17.4

ured each month. An aliquot portion of the drainage water was removed from the receptacles from time to time for analysis. Samples representing the flow between May 23 and October 1, 1910, were analyzed

January the unplanted tanks gave a much greater flow.

The composition of the drainage water in parts per million is stated in Tables II and III. The unplanted tanks show quite a constant density of

¹ Science, N. S., 29, 621-3.

total solids for both the summer and winter months. In the drainage from the unplanted tanks the bases (Ca, Mg, K, Na) have about the same density in both the summer and winter, as does also the silica. The chief difference is in the nitrates and bicarbonates, the former being much richer in winter while the latter occur in less density at that time. Determinations of nitrates in similar soils indicate very plainly that the nitrate formation occurs largely during midsummer in spite of the fact that they appear most abundantly in the winter drainage. As may be seen from Table I the flow of drainage water previous to Oct. 1 is largely spring flow and does not represent the result of the reactions that occurred in the soil during the important part of the growing season. It is quite evident that the drainage collected between Oct. 1, 1910, and May 1, 1911, will serve better as the basis for a study of the influence of vegetation on the removal of mineral matter in the drainage water.

In Tables IV and V, the substances removed in the drainage water have been calculated to pounds per acre. It will be noticed that the large differences are between the planted and the unplanted tanks. A study of the winter drainage shows:

TABLE IV.—SUBSTANCES REMOVED IN DRAINAGE WATER, POUNDS PER ACRE, MAY 23, TO OCT. 1, 1910

Tank Nos.	Crop.	Total solids.	Nitrates		Bicarbonates (HCO ₃)	Silica (SiO ₂)	Phosphates (PO ₄)	Calcium (Ca.)	Magnesium (Mg.)	Potassium (K)	Sodium (Na)
			Nitrates (NO ₃)	calculated as N.							
2, 4, 8	None	405	48.3	10.9	249	5.9	trace	66.3	10.8	1.4	19.5
3, 5, 7, 9	Maize	151	12.2	2.8	111	3.0	trace	27.6	6.8	0.4	6.2
6, 10	Oats	175	18.4	4.1	99	4.0	trace	31.8	7.8	0.4	5.8

TABLE V.—SUBSTANCES REMOVED IN DRAINAGE WATER, POUNDS PER ACRE, OCT. 1, 1910, TO MAY 1, 1911

Tank Nos.	Crop.	Total solids.	Nitrates (NO ₃)	Nitrates calculated as N.	Bicarbonates (HCO ₃)	Silica (SiO ₂)	Calcium (Ca.)	Magnesium (Mg.)	Potassium (K)	Sodium (Na)
2, 4, 8	None	2179.6	481.5	108.7	890.7	22.6	340.4	65.2	9.6	92.1
3, 5, 7, 9	Maize	649.7	35.2	8.0	446.9	11.8	130.4	23.4	5.3	53.0
6, 10	Oats	728.0	37.3	8.4	517.0	12.1	141.6	23.9	9.2	46.1

The total solids removed from the unplanted soils was three times as great as that removed from the planted soil.

The loss of nitrogen in drainage water was more than twelve times as large from the uncropped soils as from those that grew plants. Slightly over one hundred pounds of nitrogen per acre were lost from the uncropped soils during the period mentioned, while only eight pounds were lost from the cropped soils. The use of a catch crop would be of slight benefit during the fall, winter and early spring on this soil when a good summer crop is raised.

Very little more nitrogen was lost from the soil on which oats were raised than from the soil on which maize was grown, although the nitrogen in the crop was nearly fifty pounds per acre less on the oat soil.

The nitrogen in the maize crop plus that in the drainage water from the tanks cropped to maize amounted to 151 pounds per acre. That in the oat crop and drainage from the oat tanks amounted to 103 pounds per acre. There were, therefore, 48 pounds per acre more available nitrogen in the maize soil than in the oat soil. This is in line with the results of previous work by the writers which indicated either that the

maize plant has a stimulating effect on the process of nitrification or that it utilizes to a large extent nitrogen in forms other than nitrates, or that both of these phenomena occur.¹

The loss of calcium was more than twice as great from the uncropped as from the cropped soils. The difference in this constituent in the drainage when the soil was not planted, over what it was when planted, amounted to several times the quantity that was probably taken up by the crop. The decreased leaching of calcium, apparently due to the growth of plants on the soil, cannot be accounted for by absorption by the plant, but appears to be a real conservation of this constituent.

The ratio between the removal of magnesium in the drainage from the planted and unplanted soils was almost the same as that for calcium, but the total quantities were only about one-fifth as much.

Potassium was leached from the tanks only in quantities of from five to ten pounds per acre, and from the tanks on which oats were grown there was no greater loss from the uncropped than from the cropped soils. Sodium, on the other hand, was removed by drainage in quantities of from fifty to nearly

ninety pounds per acre. However, the ratio between the loss from the cropped and uncropped tanks was not so great as was the ratio for calcium.

The bicarbonates were large in amount, but the much greater loss of basic material from the uncropped than from the cropped soil was removed mainly in the form of nitrate and not as bicarbonate. Any system of soil management which results in a decreased removal of nitrates in the drainage water will probably effect a conservation of bases in the soil. The tendency of new soils in a humid region to become "sour" after being cultivated for a number of years may be explained by the abundant formation of nitrates in such soils when first tilled, and the consequent removal of corresponding quantities of calcium in the drainage water. Forest soils, in which nitrification is said to be absent, and permanent grass land, in which nitrification is hardly more than sufficient to supply the crop, doubtless lose very little calcium as compared with the same soils under the plow.

CORNELL UNIVERSITY,

ITHACA, N. Y.

¹ *J. Frank Inst.*, Jan. and Feb., 1911, pp. 1-16, 205-28.

A NEW METHOD FOR CALCULATING WATER IN CANNED TOMATOES AND THE DETECTION OF ADDED WATER TO CANNED TOMATOES.

By LEON A. CONGDON.

Received June 12, 1911.

The subject of added water to canned tomatoes having been brought up in the author's inspection work under the State Pure Food Law, he submits the following information and a new method which he has worked out.

I. TRADE STANDARD FOR CANNED TOMATOES.

The Ohio Trade Standard for canned tomatoes gives the following for grades of canned tomatoes:

Fancy.—Packed from whole red ripe tomatoes; 38 ounces gross weight and not less than 20 ounces of fruit exclusive of juice. Packed to comply with the National Pure Food Law.

Standard.—Thirty-six ounces gross weight and not less than 18 ounces of ripe fruit, exclusive of juice, not necessarily all red, and to be packed in accordance with the National Pure Food Law.

II. ANALYSIS OF PROXIMATE COMPOSITION OF CANNED TOMATOES.

According to U. S. Dept. Expr. Station, *Bulletin* 28, p. 70.

Num- ber of analysis.	Water. Per cent.	Protein. Per cent.	Fat. Per cent.	Total carbohydrates. Per cent.	Crude fiber. Per cent.	Ash. Per cent.	Fuel value per pound.
19	94.0	1.2	0.2	4.0	0.5	0.6	105

III. COMPOSITION OF TOMATO FRUIT.

According to the *Handbook of Experiment Station Work*, 1893. This is the average of over 66 varieties of tomatoes.

Water. Per cent.	Protein. Per cent.	Fat. Per cent.	Nitrogen- free extract. Per cent.	Crude fiber. Per cent.	Ash. Per cent.	Sugar. Per cent.	(Malic) acid. Per cent.
93.64	0.91	0.43	3.80	0.75	0.47	3.05	0.46

IV. AUTHOR'S METHOD AND TOMATO (CANNED) FACTORS.

(a) Separation of fruit and juice:

The gross weight of the can of tomatoes was first obtained; the can was then opened and the contents poured upon cheese-cloth (40 threads to an inch) suspended over a large funnel, the juice running into a beaker. The fruit was not crushed, but was allowed to drain as long as the juice dropped freely. The empty can was then thoroughly dried and weighed. The difference between the gross weight of the canned tomatoes and the weight of the empty can gave the net weight of the juice and tomatoes. The juice, after filtering through the cheese-cloth, was then poured into the empty can and weighed—deducting the weight of the empty can gave the net weight of the juice alone. The difference between the whole net weight of the canned tomatoes and the net weight of the juice gave the net weight of the fruit of the canned tomatoes.

(b) Water in the solids or fruit and in the juice:

Taking homogenous samples of 10 grams of the fruit and of the juice respectively, in small tared evaporating dishes, they were evaporated over the water

bath in order to lose as much water as possible, then transferred to a water oven and dried for several hours until a constant weight was obtained. Found the per cent. of solids in the fruit and in the juice, respectively, and subtracting each from 100 per cent. gave the amount of water in the fruit and in the juice.

(c) Specific gravity of the juice:

The specific gravity of the juice strained through cheese-cloth (40 threads to an inch) was taken at room temperature by the Westphal balance.

(d) Total acidity of the juice:

The total acidity of this juice was taken by titrating 25 cc. of the juice with $N/10$ NaOH, using phenolphthalein as the indicator. Multiplying the number of cc. of $N/10$ NaOH, required to titrate by 4, gave the number of cc. $N/10$ NaOH, or acidity of 100 cc. of the juice. Dividing by the specific gravity of the juice and multiplying by 0.0067 (factor for malic acid) gave the per cent. of acid expressed as malic acid.

(e) Ratio numbers or tomato (canned) factors for method of calculating water in canned tomatoes:

By dividing the specific gravity of the juice of the canned tomato, plus 0.1000, by the number of cubic centimeters of $N/10$ NaOH, required to titrate 100 cc. of the juice, gave a number which I called a ratio number or tomato juice factor. Dividing the acidity by the specific gravity plus 0.1 gave another number which I called "Ratio Number Two."

(f) Qualitative tests for salt:

Filtered the juice through filter paper, and acidifying with HNO_3 precipitated the chlorine in the salt as $AgCl$.

V. RESULTS.

The following tables show the results of analyses:

TABLE I.—SHOWING RESULTS ON AVERAGE ACIDITY, RATIOS, AND WATER.

No. of samples.	Range of average acidity $N/10$ NaOH. Cc.	Average acidity expressed in cc. of $N/10$ NaOH required to titrate 100 cc. juice.	Juice through cheese-cloth. Average specific gravity at room temperature.	Average ratio number 1 = sp. gr. + 0.1 ÷ acidity of 100 cc. juice.	Average acidity expressed as malic acid.	Average amount water in juice. Per cent.	Average amount water in tomatoes and juice. Per cent.	Average ratio No. 2, acidity as $N/10$ NaOH ÷ 0.1 + sp. gr. juice.
1	30 to 40	38.4	1.0105	0.0288	0.25	97.52	96.18	34.5
3	40 to 50	43.7	1.0152	0.0255	0.28	96.24	95.30	39.1
10	50 to 60	56.4	1.0197	0.0198	0.34	95.24	94.00	50.3
15	60 to 70	62.1	1.0231	0.0178	0.40	95.03	93.66	55.2
2	70 to 80	70.8	1.0223	0.0158	0.46	94.81	93.21	63.0
1	80	82.0	1.0242	0.0138	0.54	94.24	92.32	72.8
1	Near 80	77.6	1.0321	0.0145	0.51	92.23	90.44	65.8

TABLE II.

Capacity of can in cubic centimeters.	Number of brands.	Grade of tomatoes claimed.	Average net wt. in ounces.	Average wt. of solids or tomatoes in ounces.	Average wt. of juice, strained through cheese-cloth, as ounces.
620	1	select	20.8750	9.4375	11.4375
1000	14	extra	33.2733	16.2258	16.9475
1025	1	choice	33.1875	16.5000	16.6875
1030	1	selected	34.1875	16.5000	17.6875
1040	1	full standard	32.7500	14.7500	18.0000
1050	4	selected	35.0469	19.6875	15.3594
1070	1	fancy, selected	35.1250	20.1875	14.9375
		fancy, extra and solid			
1150	7	packed	39.6339	23.0554	16.5785
		highest excellence	39.4375	20.0625	19.3750
1165	1		40.0625	17.8125	22.2500
1170	1	solid packed	41.4375	22.1875	19.2500
1200	1	first quality			

In regard to the amount of solids or tomatoes and of the juice in canned tomatoes, the above table will give the average amounts found in my analysis of 33 brands picked up from retail markets of North Dakota.

In order to get more information on the subject of the detection of an added water to tomatoes, I analyzed a can of tomatoes to which had been added an approximate amount of water and salt. The tomatoes had been canned for a period of six months. The following is a summary of the analysis:

Capacity of can, 1030 cc. Net weight found, 35.5625 ounces. Solids, 18.2500 ounces. Juice strained through cheese-cloth, 17.3125. Per cent. water in solids, 93.21. Per cent. water in juice, 95.70. Per cent. water in solids and juice, 94.45. Specific gravity of juice strained through cheese-cloth (at room temp.), 1.0201. Acidity of 100 cc. of juice expressed in cc. *N*/10 NaOH, 75.2 cc. *N*/10 NaOH. Acidity of 100 grams juice expressed in per cent. of malic acid, 0.49 per cent. "Ratio Number I" = $-0.1000 + \text{sp. gr. juice} \div \text{acidity of 100 cc. juice} = 0.0148$. Specific gravity juice free from suspended matter (at room temp.), 1.0196. Corrected "Ratio Number" of juice free from suspended matter, 0.0148. Relation per cent. of water of solids to per cent. water of juice or per cent. water solids = per cent. water juice = 0.973.

In this can of tomatoes of "Earlianna Variety," approximately 3.13 per cent. water was added before canning the tomatoes and they were heated just enough to sterilize them for canning. Salt was added to season the tomatoes in good shape.

A NEW METHOD FOR CALCULATING WATER IN CANNED TOMATOES.

The following is a formula which will calculate the per cent. water found in canned tomatoes. It is based on "Ratio Number Two" as described in the methods used by the author. This "Ratio Number Two" which is the acidity of 100 cc. of the juice expressed in cc. of *N*/10 NaOH, divided by 0.1 plus the specific gravity of the juice strained through cheese-cloth (40 threads to the inch). Subtract this "Ratio Number Two" from the acidity of 100 cc. of the juice expressed in cc. *N*/10 NaOH; the difference so obtained taken from 100 per cent. gives the per cent. of water found in the canned tomatoes.

∴ One hundred per cent. — (acidity — "R. N. Two") = per cent. of water in canned tomatoes.

TABLE III.—COMPARISON OF THIS METHOD WITH THE METHOD OF DRYING IN WATER OVEN.

Number of samples.	Average acidity. Cc.	"Ratio No. Two."	Acidity minus "R. N. Two."	Per cent. water by formula.	Per cent. water by drying in oven.	Difference of two methods.
1	38.4	34.5	3.9	96.1	96.18	—0.08
3	45.7	39.1	4.6	95.5	95.30	0.20
10	56.4	50.3	6.1	93.9	94.00	—0.10
15	62.1	55.2	6.9	93.1	93.66	—0.56
2	70.8	63.0	7.8	92.2	93.21	—1.01
1	77.6	65.8	11.8	88.2	90.44	—2.34

CALCULATING WATER ORIGINALLY ADDED TO CANNED TOMATOES.

In the sample of canned tomatoes which I knew to have about three per cent. water originally added,

the "Ratio Number One," which was the specific gravity + 0.1 divided by the acidity, was found to be 0.0144. Subtract this "Ratio Number One" from the "Ratio Number One" of the canned tomatoes to be examined, and multiply by 3—gives the per cent. of water originally added to the tomatoes.

Expressed as formula: ("R. N. One" — 0.0144) 3 = per cent. water originally added to canned tomatoes.

TO FIND THE EXCESS OF WATER ACTUALLY FOUND ADDED.

(Exclusion of cold-packed tomatoes.)

Formula: Per cent. water found — 90.44 per cent. = excess water found added. (90.44 per cent. = average per cent. water in canned tomatoes of right acidity.)

By previous tables the average amount of water can be seen to be from 90.44 per cent. to 96.18 per cent. in the tomatoes and juice. Therefore the highest amount of excess water found added was a little over 5 per cent. By the following explanation it can be readily seen how this excess of water came to be added.

SALT IN CANNED TOMATOES.

The effect of added salt to canned tomatoes caused a higher specific gravity of the juice; and also a higher per cent. of solids of both pulp and juice, thereby lowering the per cent. of added water. I understand that canning factories add salt to the tomatoes before canning, in the shape of salt solution or "brine" as it is called. The "brine" is added to the tomatoes in the storage vat before canning. This is claimed to keep the tomatoes until they are ready for canning. A representative of a certain wholesale house told me that on inspecting some of their best brands of tomatoes, he has found them to contain entirely too much salt and enough to affect the taste of the fruit. Of the 33 different brands of tomatoes examined by me, I found them all to contain salt as sodium chloride. Nine brands contained a considerable amount of salt, three brands a medium amount of salt, and twenty-one brands an ordinary amount of salt. The salt could not be detected by taste, but was detected by chemical means.

By the above statement, water is at least added in the form of a solution of salt or "brine" as sodium chloride solution.

Quantitative determinations of salt in canned tomatoes average 0.14 per cent.

Since the previous tabulations on 33 different cans of tomatoes analyzed, I analyzed 25 more different cans of tomatoes of different grades. The following tables will give the average determinations of these 25 more determinations.

TABLE IV.

Number of samples.	In 100 cc. juice. Average acidity expressed as cc. <i>N</i> /10 NaOH	Average sp. gr. of juice through cheese cloth.	Average per cent. of H ₂ O in tomatoes and juice by drying in water oven. Per cent.	Average per cent. of H ₂ O by author's formula	Average per cent. of ash in canned tomatoes which includes the salt.
3	45.7	1.0163	94.83	95.2	0.39
12	57.0	1.0187	94.49	93.9	0.44
9	63.1	1.0196	93.63	93.2	0.47
1	70.4	1.0210	94.10	92.4	not determ.

TABLE V

Capacity of can in cubic centimeters.	Number of brands or samples.	Grade of tomatoes claimed.	Average net weight in ounces.	Average weight of solids or tomatoes in ounces.	Average weight of juice in ounces (strained through cheese-cloth)
Cc.					
1000	11	hand-packed, selected and first quality	34.6420	18.0454	16.5966
1150	2	selected quality	37.9375	21.8437	16.0938
1000	12	cold-packed	33.6302	21.2708	12.3594

AMOUNT OF WATER SHAKEN OUT OF TOMATOES BY
TRANSPORTATION HALF WAY ACROSS
THE CONTINENT.

Through the courtesy of H. B. Messenger, of Federalsburg, Md., I was able to make some experiments with tomatoes which were canned by him the latter part of 1910. These cans of tomatoes had stood in the warehouse until the early spring, when 36 cans were removed as being average samples of the product then on hand. Twelve cans were opened and examined by Mr. Messenger and associates, and the remaining 24 cans were packed in a case and shipped to the Food Commissioner here at Fargo, North Dakota. The Food Commissioner submitted 12 of these cans of tomatoes to me for analysis, and the remaining 12 cans were sent back to Maryland to be examined by the packers.

The following is a comparison of the mean weight of the 12 cans of tomatoes analyzed before shipment and of the 12 cans of tomatoes after shipment:

	Net weight. Ounces.	Solids. Ounces.	Liquid. Ounces
As shipped.....	33.16	19.83	13.33
As received.....	33.496	17.425	16.265

The method of analysis used by the writer was the same as that used by the factory and was established by the Cannery Association:

"Contents of can drained on $\frac{1}{4}$ -inch mesh flat screen for two minutes." The amount of fluid draining through at this period of time was then weighed. The tomatoes left on screen were found by deducting the weight of the juice from the net weight of the contents of the can.

It can be plainly seen that the average amount of tomatoes disintegrated by transportation for such a long distance was 2.935 ounces, or practically 3 ounces, thus about 9 per cent. by weight. I also analyzed these same 12 cans of tomatoes by my method of draining through the cheese-cloth of 40 threads to the inch, and I found the difference of the two methods in favor of the packer or canner, as regards the amount of liquid draining through. The average comparison between the $\frac{1}{4}$ -inch screen method and the cheese-cloth method is as follows:

COMPARISON OF SCREEN AND CHEESE-CLOTH METHODS.

One-fourth-inch screen (drained 2 minutes).		Cheese-cloth, 40 threads to inch. (About 2-hour drain.)		Credit in tomatoes. to packer.
Tomatoes. Ozs.	Liquid Ozs.	Tomatoes. Ozs.	Liquid. Ozs.	
17.425	16.071	21.014	12.482	3.589

It can be readily seen that by this method of draining through cheese-cloth, the amount of tomatoes broken up by transportation or jarring is given credit to the packer, and is 3.589 ounces, or practically 4

ounces, thus about 12 per cent. by weight. Now the proximate amount of water which is shaken out by transportation can be calculated. It is shown by the above that 9 per cent. (by weight) of the tomatoes were disintegrated by transportation, and 12 per cent. (by weight) of the tomatoes were found disintegrated by the cheese-cloth method. As the cheese-cloth method leaves a filtrate which is practically free from suspended matter, the difference between 12 per cent. and 9 per cent. gives the amount of water shaken out of the tomatoes by transportation, or 3 per cent.

SUMMARY.

1. The average acidity of 46 samples out of 58 samples of canned tomatoes analyzed was within the range of 50 cc. $N/10$ NaOH to 70 cc. $N/10$ NaOH for 100 cc. of the juice, the average acidity being 59.7 cc. $N/10$ NaOH for 100 cc. of the juice for these 46 samples.

2. The average specific gravity of the juice of the canned tomatoes strained through a cheese-cloth of 40 threads to the inch was:

One sample, 1.0105, at room temperature by Westphal balance.

Six samples, 1.0157, at room temperature by Westphal balance.

Twenty-two samples, 1.0192, at room temperature by Westphal balance.

Twenty-four samples, 1.0213, at room temperature by Westphal balance.

Four samples, 1.0241, at room temperature by Westphal balance.

One sample, 1.0242, at room temperature by Westphal balance.

Taking the 46 samples which has a very close acidity the specific gravity was very close and the average specific gravity of these 46 samples was 1.0202° at room temperature.

3. The amount of water in the canned tomatoes for the 58 samples analyzed varied from a range of 90.44 per cent., the lowest, to 96.18 per cent., the highest amount found present by drying in the water oven. The average amount of water of the 46 samples, which were very constant in regard to the acidity and specific gravity, was found also to be rather constant in regard to the per cent. of water. This amount averaged 93.95 per cent. water.

4. The majority of the cans of tomatoes were of 1000 cc. capacity. There were 37 of this capacity out of a total sum of 58 brands examined. Twelve of these 37 brands were the so-called "cold-packed."

Twenty-five of the 1000 cc. capacity can tomatoes had an average net weight of 33.9576 ounces of which an average of 17.1356 ounces were tomatoes and an average of 16.7720 ounces were juice.

The 12 "cold-packed" variety of canned tomatoes examined had a capacity of 1000 cc. The average net weight of these was 33.6302 ounces of which an average of 21.2708 ounces were tomatoes and an average of 12.3594 ounces were juice.

5. A method was obtained by which water could be calculated in the canned tomatoes. The method

was based on the acidity and specific gravity of the canned tomato juice.

The formula used was as follows:

One hundred per cent. minus (acidity minus "Ratio Number Two") = per cent. of water in canned tomatoes.

The formula gave lower results—the range being from 0.08 per cent. to 2.34 per cent., but the general average was 0.5 per cent., or smaller, higher results being found by drying in the water oven, due perhaps to the changing of some of the solid material while in the process of dehydration in the water oven.

6. A small amount of water was found added to the canned tomatoes in the form of a solution of NaCl or common salt, the *greatest amount* found added being about 5 per cent. water. The amount of water in canned tomatoes of the correct acidity was found to be 90.44 per cent., in the case of tomatoes not cold-packed. In the case of tomatoes which were cold-packed, the acidity was, of course, a trifle lower (about 10 cc. $N/10$ NaOH less for 100 cc. juice) and the amount of water was found to be on the average about 95.23 per cent. by water oven and by formula to be 94.03 per cent. The correct acidity was based on analyses of about 66 varieties of tomatoes. The acidity of canned tomatoes should be higher and the water content lower, due to loss in sterilization. This, of course, is not the case so much in cold-packed tomatoes.

7. Taking the foregoing summary into consideration, the inference one draws should be of importance to both the tomato packer and to the pure food official.

First, there are very few cans of tomatoes which come within the trade standard for "Standard" tomatoes, to say nothing of the so-called "1st Quality" brands of tomatoes. It can be readily seen from the average amount of tomatoes that is put up in a can, that packers are putting about one-half a can of tomatoes to about one-half a can of juice.

Second, if the juice of the can of tomatoes falls below a specific gravity of 1.0130 at room temperature, added water is sure to be present; and if the specific gravity of the juice, filtered through cheesecloth of 40 threads to the inch, falls below 1.0200 at room temperature, added water is suspected.

Third, the acidity of the canned tomato juice expressed in number of cc. of $N/10$ NaOH should not fall below 50 cc. $N/10$ NaOH for 100 cc. of the canned tomato juice. If the acidity is less than this, added water is sure to be present; if the acidity of the canned tomato juice is less than 78 or 79 cc. $N/10$ NaOH, added water is suspected.

Fourth, since the annual pack of tomatoes in the United States is probably not less than 10,000,000 cases, canned tomatoes are an important article of food for us to consider.

Fifth, the amount of water shaken out of the tomatoes by transportation half way across the continent was practically one ounce, from the cans of tomatoes of the net weight of 33 ounces or a little over 3 per cent. by weight.

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CIDER VINEGAR.

By FRANK E. MOTT.

Received June 20, 1911

The purpose of this article is to describe a method whereby certain forms of adulteration of cider vinegar, now being practiced by the vinegar manufacturer, may be detected.

The method depends upon the relation between levulose and dextrose in pure cider vinegar, as computed from the percentage of reducing sugars, expressed as dextrose, and the polarization, degrees Ventzke, 200 mm. tube, 20° C.

PART I.

It is now a common practice among vinegar manufacturers to compound and sell as cider vinegar a spurious article, made by adding to the legitimate fermented product of pure apple juice, dilute HAc or H_2O which contain as dissolved solid material about 2 per cent. of solids derived from boiled cider, or the evaporated extract from re-pressings, apple parings, skins, cores, etc.

When a sufficient quantity of the the boiled cider or apple waste extract has been added to pure cider vinegar, the adulteration may be detected by the positive polarization at 20° C., stable after inversion, as is shown by the analysis given in Table I:

TABLE I

Total solids.	Ash.	Character of ash.	R Sugars.		P_2O_5 , mg.		Non-sugar solids.	Polarization, °V., 20° C., 200 mm. tube	
			Before inv.	After inv.	Soluble.	Insoluble.		Before inv.	After inv.
			1.13	1.13	14.3	7.3	1.21	+0.2	+0.2

Here the non-sugar solids are so low as to engender suspicion, but have been found equally as low in pure cider vinegar, and the other values, taken separately, excepting the polarization, are such as have also been found in pure cider vinegar. The polarization alone shows specifically that the vinegar has been adulterated with foreign dextrorotary material.

The manufacturer of adulterated cider vinegar can, however, seldom be caught in the manner cited in the preceding paragraph. He sees to it that his illegitimate product keeps pace with the progress of the government chemist, and that it continues to bear all the characteristics of pure cider vinegar as generally accepted. Such products, some made by the manufacturer of the spurious article mentioned in Table I, who stated that the article mentioned in Table I was an accident, are shown by the analyses given in Table II:

TABLE II

Total solids.	Ash.	R sugars	P_2O_5 , mg.		Non sugar solids.	Polarization, °V., 20° C., 200 mm. tube	
			Soluble.	Insoluble.		Before inv.	After inv.
			14.2	8.8	1.77	+0.0	+0.0
2.50	0.32 (normal)	0.728	14.2	8.8	1.77	+0.0	+0.0
2.30	0.33	0.733	12.0	7.3	1.57	-0.6	0.6
2.67	0.32	0.688	11.8	6.5	1.98	-0.2	-0.2
2.75	0.36	0.682	11.0	6.2	2.06	-0.2	-0.2
2.76	0.34	0.688	11.7	6.3	2.07	-0.2	-0.2

¹ References at the end of the paper. see (1).

The analyses given in Table II are fairly illustrative of many articles sold to-day as pure cider vinegar. Here every value, excepting the polarization of sample I, taken by itself, is such as has been found in cider vinegar of known purity, and the products have to be passed as conforming to the requirements of a "legitimate fermented product of pure apple juice." These products were adulterated with apple-waste extract. Later in this article will be shown a method for the detection of this form of adulteration, and the method will be applied to the analyses given in Table II.

PART II.

THE RELATION BETWEEN LEVULOSE AND DEXTROSE IN PURE CIDER VINEGAR.

Essentially, the sugars naturally present in pure cider vinegar are levulose and dextrose: levulose, as such, and levulose and dextrose as invert sugar, resulting from the complete inversion of the sucrose originally present in the apple juice.

C. A. Browne, Jr.,² has shown that, in a mixture of levulose and dextrose, the percentage of each sugar present may be computed from the polarization and the percentage of reducing sugar, expressed as dextrose. The formulae derived by Browne are best applicable to the conditions under which they were derived, namely, solutions of pure sugars, but this article will show that a practical application of the formulae may be made in the computation of the percentages of levulose and dextrose present in cider vinegar.

The formulae derived by Browne in the above-mentioned article are:

$$\text{I. Levulose (L}_{20^{\circ})} = \frac{0.793 R - P}{2.08}$$

where R equals per cent. of reducing sugars, as dextrose, and P is the polarization, degrees V., 20° C., 200 mm. tube, on a basis of 26.048 grams in 100 cc.

II. Dextrose (D) = R - 0.915 L., R and L having the significances above mentioned.

For the derivation of these formulae, reference is made to the previously cited article of Browne.

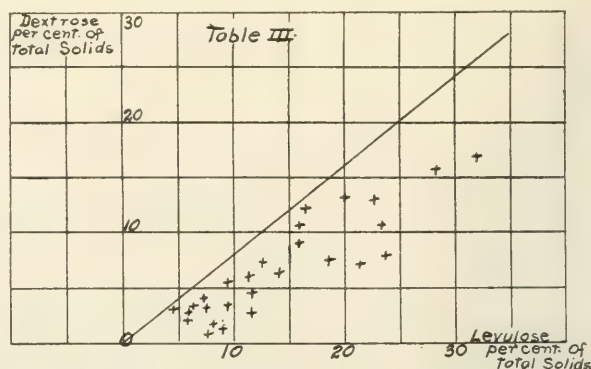
In applying the formulae of Browne to the computation of levulose and dextrose in cider vinegar, the author proceeds thus:

$$P = \frac{p \times 26.048}{\text{total solids}}$$

where P equals the value to be substituted in formula I, and *p* equals the corrected polarization °V of vinegar, clarified with subacetate of lead, at 20° C. in a 200 mm. tube. R equals the per cent. of reducing sugars as dextrose (r) in the total solids, and is the value to be substituted for R in formulae I and II.

Making use of the above formulae, the percentages of L and D were calculated in all the reliable published analyses of cider vinegar of known purity,³ which give the necessary data for computation, that the author is familiar with, and from the values so obtained D as ordinate was plotted against L as ab-

scissa, and the maximum value for D so obtained is represented by the line shown in Table III.⁴



All the D values computed from reliable published and unpublished analyses of pure cider vinegar lie below this line of maximum value for D, from which it was concluded that whenever in analysis of cider vinegar a value for D is found in excess of the maximum value for D, as shown by the line in Table III, to correspond to the L value found by analysis, then foreign dextrorotary material is present.

As a check upon the values, computed by the formulae of Browne, for L and D, the following method was employed: From the fact that in pure cider vinegar the percentage of L, as computed by the formulae of Browne, always exceeded the percentage of D, it was reasoned that at 87° C., when $\alpha_D L$ equals $\alpha_D D$, pure cider vinegar would be laevorotary, and the rotation measured, though influenced to some extent by substances present other than L and D, could be used to calculate, at least approximately, the percentage of L in excess of the percentage of D. And that, *vice versa*, cider vinegar adulterated with apple-waste extract, etc., in amount sufficient to bring the percentage of D in excess of that of L, would at 87° C. polarize to the right, though at 20° C. it might to the left, and that the polarization so measured could be used to compute approximately the percentage excess of D over L. Table IV shows the experimental results so obtained:

TABLE IV.

Pure cider vinegar.		Cider vinegar plus apple waste.	
Per cent. excess L over D by formulae of Browne.	Per cent. excess L over D calculated from polarization at 87° C.	Per cent. excess D over L by formulae of Browne.	Per cent. excess D over L calculated from polarization at 87° C.
2.1	2.5	7.4	7.3
4.0	4.6	3.6	3.2
8.0	8.3	2.3	2.7
12.6	13.0	1.5	1.8
		0.0 Pol. °V, ± 0.0 87° C.	

In preparing Table III, the author noticed that the ratios D/L as obtained from his own analyses were fairly constant, while the ratios obtained from the published analyses varied greatly, but at the time he thought the variation a natural one. Later, in discussing this paper with H. C. Lythgoe, Analyst of the Mass. State Board of Health, mention was made of the influence of aldehydes on the reducing power of vinegar, thus opening a line of thought in pursuit

of which the author observed that the value for R sugars as obtained in his own analyses was by the method given under reference (1), eliminating the aldehyde error, while the values for R sugars in the published analyses were obtained directly upon the vinegar by the official method, and contained the aldehyde error. A comparison was then made between the percentage excess of L over D, in 5 samples of known-purity cider vinegar, as computed by the formulae of Browne, using the official method for R sugars containing the aldehyde error, and the percentage excess of L over D as computed from the polarization at 87° C., 200 mm. tube. The results so obtained appear in Table V:

TABLE V.

Variety.	Per cent. L in total solids.	Per cent. D in total solids.	By formulae of Browne, per cent. excess L over D.	Per cent. excess L over D, from P, at 87° C.	Polarization, 200 mm. tube.	
					87° C.	20° C.
Baldwin.....	24.6	17.4	7.2	10.9	-0.5	-1.2
King.....	23.1	15.0	8.1	11.8	-1.1	-1.9
Greening.....	26.4	14.6	11.8	13.9	-1.0	-2.2
Russet.....	19.8	15.1	4.7	7.2	-0.6	-1.2
Mixed, pressing..	17.5	12.9	4.6	8.6	-0.5	-1.0

In Table V, the discrepancy between the percentage excess of L over D, as computed by the formulae of Browne, and the percentage excess of L over D as estimated from the polarization at 87° C., is too great to be due to experimental error. Such a discrepancy would be produced by the substitution of too large a value for R in the formulae of Browne.

A comparison was then made between the percentage excess of L over D as calculated by the formulae of Browne in the same 5 samples of cider vinegar as were used in preparing Table V, using, however, the value for R sugars obtained by the use of the method given under reference (1), and the percentage excess of L over D as computed from the polarization at 87° C., 200 mm. tube. This comparison appears in Table VI:

TABLE VI.

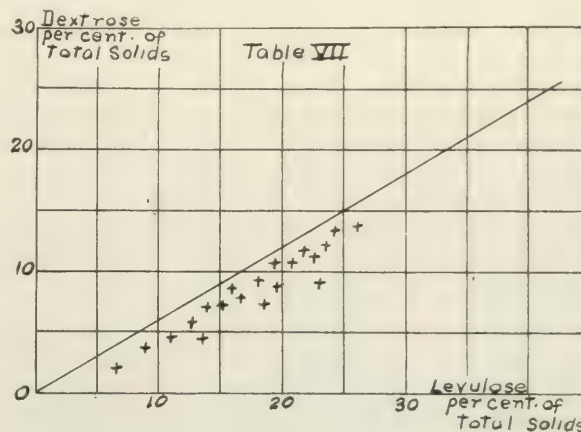
Computed by formulae of Browne.

Variety.	Per cent. L in total solids.	Per cent. D in total solids.	Per cent. excess L over D.	Per cent. excess L over D, from P, at 87° C.	Polarization, 200 mm. tube.	
					87° C.	20° C.
Baldwin.....	19.7	8.8	10.9	10.9	-0.5	-1.2
King.....	18.7	7.4	11.3	11.8	-1.1	-1.9
Greening.....	23.1	9.1	14.0	13.9	-1.0	-2.2
Russet.....	16.0	8.6	7.4	7.2	-0.6	-1.2
Mixed, pressing..	14.2	7.1	7.1	8.6	-0.5	-1.0

The very satisfactory agreement between the percentage excess of L over D as computed by the formulae of Browne, using for R the value with the aldehyde error eliminated, and the percentage excess of L over D as computed from the polarization at 87° C. is evident. The same good agreement is obvious in Table IV, where values for the excess of L over D by the formulae of Browne were calculated by substituting for R the value with the aldehyde error

eliminated. Thus it is concluded that the proper relation between L and D is obtained by the use of the formulae of Browne only when the value for R substituted in the formulae is the value with the aldehyde error eliminated in some such way as in the method given under reference (1).

In Table VII is shown the line which represents the maximum value for D corresponding to any value of L. This line was obtained by plotting the values obtained by computing L and D in 20 different samples of known-purity cider vinegar, using the formulae of Browne and a value for R having the aldehyde error eliminated.



In Table VII, crosses indicate the results actually obtained in analysis.

Application of the method employed in the computation of the values used in the plotting of Table VII was then made to the analyses given in Table II. The results so obtained appear in Table VIII:

TABLE VIII.

Computed by the formulae of Browne.				Per cent. excess D over L, from P, 200 mm.		
Per cent L in total solids.	Per cent. D in total solids.	Per cent excess D over L.	Per cent. excess D over L, from P, at 87° C.	87° C.	20° C.	
11.1	19.0	7.9	8.0	+0.6	±0.0	
15.5	17.8	2.3	0.0	±0.0	-0.6	
10.8	15.9	5.1	5.0	+0.4	-0.2	
10.4	15.3	4.9	4.9	+0.4	-0.2	
10.4	15.3	4.9	4.9	+0.4	-0.2	

In these samples it was then seen that D was in considerable percentage excess over L and the adulteration with foreign dextrorotary material was apparent. The manufacturer of these vinegars admitted adulteration with so-called boiled cider.

DISCUSSION OF RESULTS.

The line plotted in Table III represents an approximate relation between L and D in pure cider vinegar. That the relation thus represented is only approximate is shown by the discrepancy between results for the percentage excess of L over D, as obtained by two different methods of calculation and given in Table V. That this discrepancy is due to the incorrect value for R, substituted in the formulae of Browne, is shown by the results given in Table VI.

In plotting the line given in Table VII, where the values for L and D were computed by the formulae

of Browne, using for R a value with the aldehyde error eliminated, and checking the values so obtained by calculation of the percentage excess of L over D from the polarization at 87° C., it is seen that the grouping of results is far more uniform than in the plot in Table III.

Polarization at 87° C. cannot be recommended as a general method for the determination of the percentage excess of one sugar over another in cider vinegar. The reading at 87° C. is frequently so close to zero that the instrumental error is very great. All the readings at 87° C. given in this article are the average of 9 settings of the instrument. In most cases the agreement between the two methods of calculation is fairly satisfactory, but in at least one instance, No. 2 in Table VIII, the agreement was far from satisfactory, the percentage excess of D over L by the formulae of Browne being 2.3, while the average value of the polarization at 87° C. was ± 0.0 for 9 settings of the instrument. It may, however, be stated very positively that wherever an article, purporting to be cider vinegar, polarizes to the right at 87° C., then the article has been adulterated with foreign dextrorotary material.

SUMMARY.

Assuming that the sugars naturally present in pure cider vinegar are essentially levulose and dextrose:

1. A relation exists between the levulose content and the dextrose content of pure cider vinegar.

2. It is believed that the line given in Table VII represents with reasonable precision the true relation between L and D in pure cider vinegar. This line is based upon 20 analyses of pure cider vinegar made by the author. Computed from the reliable analyses of pure cider vinegar at present available, about 150 of which give the necessary data, if the aldehyde error be eliminated all the L and D values lie below this line.

3. Whenever a cider vinegar polarizes to the right at 87° C., sucrose being absent, the vinegar has been adulterated with foreign dextrorotary materials, usually dextrose. Cider vinegar may be adulterated with foreign dextrorotary material and yet polarize to the left at 87° C.

4. Whenever a value for D is found in a cider vinegar in excess of the maximum value for D, as indicated by Table VII, to correspond to the value of L found by analysis, the sample is not exclusively the fermented product of pure apple juice, but, sucrose being absent, has been adulterated with foreign dextrorotary material, usually dextrose.

5. The method finally adopted by the author for the determination of the relation between L and D in cider vinegar is as follows:

Determine the absence of sucrose by polarization before and after inversion.

Total Solids.—Place 10 cc. of the vinegar in a platinum dish, flat bottom, about 60 mm. in diameter, and evaporate to dryness on a boiling water bath. Add 5 cc. water and again evaporate to dryness. Again add 5 cc. water and evaporate, allowing the dish to remain on the water bath about 1 hour after

the final evaporation. Remove the dish; dry it on a towel and place in a hot air oven at 100° C. for 5 minutes. Place the dish in a desiccator, and, when cold, weigh, thus obtaining the total solids.

Reducing Sugars.—Determine the reducing sugars as follows: To the total solids in the platinum dish add about 25 cc. of water and place on the water bath until the solids are dissolved. Rinse the contents of the dish into a 100 cc. graduated flask; cool, neutralize, and make up to the mark. In the solution thus obtained, determine reducing sugars by using the Munson and Walker⁵ method on 50 cc. Express reducing sugars as dextrose.

Polarization.—To 50 cc. of the vinegar add 5 cc. lead subacetate solution, 1.25 sp. gr., two teaspoonfuls of animal charcoal, of a lot, the applicability of which to clarification for the purpose of polarization has been tested, and filter. Polarize in a 200 mm. tube at 20° C., and express as degrees Ventzke, corrected.

$$\text{Calculation. } \times L = \frac{0.793 R - P}{2.08}, \text{ where } R \text{ is}$$

the per cent. of reducing sugars, as dextrose, in the total solids, the aldehyde error eliminated. And

$$P = \frac{p \times 26.048}{\text{total solids}}, \text{ where } p \text{ is the polarization of the}$$

vinegar as obtained under "Polarization" above.

Finally, $D = R - 0.915 L$, R and L having the significances previously mentioned.

In conclusion, the author wishes to express his appreciation of the kindness of Mr. H. C. Lythgoe, Analyst of the Mass. State Board of Health, and of Professor James O. Jordan, Inspector of Milk to the City of Boston, who criticized this article previous to publication.

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4. Value for R used in computation of this plot was that given in the published analyses. Such values contain an aldehyde error, and in the results for L and D thus obtained are only approximate.
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LABORATORY OF THE BUREAU OF
MILK INSPECTION, HEALTH DEPART-
MENT, CITY OF BOSTON, MASS.,
June 7, 1911.

LABORATORY STUDIES OF PEPSIN, PANCREATIN AND COMBINATIONS OF THESE FERMENTS.

By A. ZIMMERMAN.

Received Aug. 28, 1911.

Having for some time entertained the belief that certain hitherto generally accepted statements relative to the pharmacology and therapeutic value of pepsin and pancreatin were erroneous, the writer decided to conduct certain laboratory experiments to determine, if possible, whether these statements should be accepted as scientifically correct.

¹ Read before Division of Pharmaceutical Chemists, American Chemical Society, June Meeting.

The results of these studies, together with the conclusions deduced, are given below.

The U. S. Pharmacopeia, 8th revision, under the heading "Pepsin," states that "pepsin and pancreatin are incompatible with each other; if the solution be neutral or alkaline, the pancreatin gradually destroys the pepsin, and, if acid, the pepsin destroys the pancreatin."

Under the heading "Pancreatin" it is said "the digestive power of pancreatin is injured in contact with pepsin solution."

This supposed incompatibility of pepsin and pancreatin in the same solution has been the subject of numerous articles in medical and pharmaceutical journals, notably that of the Council on Pharmacy and Chemistry of the American Medical Association in their widely distributed article entitled "Digestive Impossibilities," the conclusions of which are in accord with those given in the U. S. Pharmacopeia.

The results of the writer's investigations and experiments seem to show that these ferments (pepsin and pancreatin) *exercise no destructive action upon one another and that with the proper degree of acidity they can be kept in the same solution, permanently for 2½ years at least, the length of time these investigations extended (Oct. 24, 1908, to date), the loss of activity noted by other observers having been due, entirely, to the reaction of the solution and to the degree of such reaction.*

The following is a general recital of the experimental work referred to.

The solutions of the digestive ferments were all prepared with equal volumes of glycerin and water, which is an excellent preservative for this class of substances. In aqueous solution alkalies and acids are more destructive to pancreatin than in this glycerin and water solution.

Pancreatin.—This ferment was prepared in ten per cent. solution with different proportions of HCl to find the proportions which would not destroy the amylopsin content, the solvent being equal volumes of glycerin and water.

The amylopsin of pancreatin is destroyed in a fifty per cent. volume glycerin-hydrochloric acid solution, when the strength is above 0.075 per cent., volume, absolute acid, the rapidity of destruction depending upon the amount of increase in acid above this point.

A solution containing 0.050 per cent., by volume, absolute hydrochloric acid, one year old, when tested according to the U. S. P. required seven minutes instead of five minutes there given for the end reaction. *By increasing the acid content to 0.075 per cent., the reaction took place within five minutes. Another specimen, three years old; containing 0.075 per cent., by volume, acid, complies with the U. S. P. test. Another, two and one-half years old, containing 0.108 per cent., by volume, acid, required 20 minutes before the reaction was no longer blue. Another, two and one-half years old, containing 0.35 per cent., by volume, acid, required 20 hours before the reaction was no longer blue. The last, containing 0.65 per cent., by volume, acid, was without action upon*

the starch, the amylopsin having been completely destroyed after three months' keeping. The pancreatic solutions made alkaline with bicarbonate of soda, adding one-half per cent., one per cent. and two per cent., respectively, after two and one-half years, were permanently active in both amylolytic and proteolytic action. These solutions, when freshly prepared and when tested now, require 15 minutes to conform to the U. S. P. reaction. *All the solutions, when made faintly acid with HCl to 0.075 per cent., required five minutes for the U. S. P. test upon starch.* In the glycerin water solution the sodium bicarbonate is much less destructive than in aqueous solution.

Note.—(Pancreatin will convert twice as much of the potato starch as it will of corn starch; with corn starch the pancreatin apparently converts the greater part rapidly, but when near the end of the reaction the last portions are very resistant, and converted with difficulty. This is probably caused by the outer membrane of the corn starch being more resistant to the action of the pancreatin than the finer, more delicate membrane of the potato starch granules.)

(In comparing diastase of malt with pancreatin, it was found to be quite as sensitive to acids, being just as readily destroyed. The destructive action of HCl is much intensified with elevation of temperature.)

Acid of 0.10 per cent. strength volume absolute hydrochloric, containing no glycerin, destroys the amylopsin of the pancreatin and the diastase of malt in one-half hour at 100° F. When kept at 70° F., the action is very much slower.

In acting upon starch, pancreatin is active and changes starch more rapidly at a lower temperature (100° F.) than the diastase of malt.

The table of tests, No. 1, appended, shows the destructive action of acids and alkalies respectively upon the amylopsin of pancreatin, in watery solution.

The trypsin is permanent in all the fifty per cent. volume glycerin solutions above referred to, made alkaline with bicarbonate of soda, or made acid with HCl up to 0.35 per cent. absolute acid. This is slightly higher than the normal acidity of the gastric juice. Above this point of acidity there is gradual destruction.

The trypsin activity of pancreatin upon milk (provided a perfectly sterile pancreatin is employed),¹ in the proportions given in the U. S. P., requires about 7 hours for complete digestion when tested by mixing one cc. of the milk mixture with nine cc. distilled water; upon adding one cc. conc. nitric acid, no precipitate or coagulum should form within fifteen minutes. No peptic or pancreatin digestion of proteids is ever so complete, even when continued for several days, as to prevent the formation of a slight precipitate when nitric acid is added to a concentrated solution.

¹ The commercial powdered pancreatin is contaminated with bacterial ferments of butyric acid. A 50 per cent. glycerine water extract of the fresh hog pancreas, filtered (glycerol pancreatin), is sterile and more reliable for digesting the proteins of milk. Macerating powdered pancreatin in 0.35 per cent. HCl renders it sterile for its proteolytic action upon milk.

The table of tests (No. 2) appended, shows the action of HCl, in varying strength, upon the trypsin of pancreatin.

Pepsin.—Commercial powdered (precipitated) pepsin contains between one per cent. and two per cent. HCl (by volume absolute); scale pepsin from three per cent. to six per cent. and pancreatin from one-half per cent. to one per cent.

This acid seems to be closely bound to the ferments, and their proteid constituents, and was estimated by making solution of the ferments in distilled water and titrating it with alkali, with litmus as indicator, calculating the total acidity as hydrochloric. Methyl orange and phenolphthalein are not so reliable. Pepsin, for permanent solution, requires an acid reaction; this was found, by experiment, to be extremely low. A solution containing 0.040 per cent., by volume, absolute HCl and pepsin of 1-3000 strength, after six months' keeping, showed 1-2750, and after nine months 1-2500, and after two and one-half years 1-1000. Increasing the acidity to 0.075 per cent. the pepsin has continued to manifest its full activity, 1-3000, after two and one-half years' keeping.

The pepsin tests were all conducted at 125° F., as directed by the U. S. P., and also at 104° F. At the lower temperature the time required for complete solution of the albumin was about double the time required at 125° F.

Pepsin is rapidly destroyed in alkaline solution, more slowly in neutral solution.

Pepsin and Pancreatin Combined.—Solutions containing ten per cent. each pepsin and pancreatin, containing HCl in graduated strength, from 0.075 to 0.65 per cent. volume absolute, after two and one-half years, have retained their full pepsin activity. Those containing less than 0.35 per cent. have retained their full trypsin activity, and those of 0.075 per cent. have retained in full the amylopsin activity with that of the trypsin and pepsin.

Some of the solutions were prepared with pepsin, rennin and pancreatin in which the conditions and results were the same as those without the rennin.

Conclusions.—If the experiments and reactions described above are considered solely by themselves, it would appear that the amylopsin of pancreatin administered by the mouth is rendered inert by the gastric juice.

The writer firmly believes, however, that such is not the case, for the following reasons:

When a mixture of animal and vegetable food is taken into the stomach, *it combines with and neutralizes the HCl of the gastric juice, the combined acid under such circumstances having no reaction on the amylopsin ferments, and for this same reason the ptyalin of the saliva is probably active in the stomach* (see Austin, *Boston Med. and Surg. Jour.*, April 6, and June 29, 1899).

The following experiments tend to show that the amylopsin of the pancreatin is not destroyed in the stomach.

When HCl in dilute form is digested with albumin, there is no solution of the latter; if, however, a small quantity of pepsin is added, solution is effected at

once, and when solution is complete, the albumin has been dissolved as an acid salt of albumin, and this before practically any digestion or conversion into albumose has taken place.

This reaction may be observed in the U. S. P. pepsin test by preparing, also, a control tube, containing only the albumin and the acid, in the proportions there given, without the addition of the pepsin. The pepsin, therefore, appears to act as a catalytic agent to bring about this combination of acid and albumin before real digestion begins. If there is added to the acid fluid, double the quantity of albumin and pepsin directed in the U. S. P. and digestion continued for two and one-half hours, it will be found that if pancreatin is dissolved in this fluid, separated from the excess of undissolved albumin and kept at 100° F. for an hour, it will have retained its full amyolytic activity.

The above would seem to indicate, very clearly, that the acid of the gastric juice, in the stomach, combines with the proteids and is no longer destructive to the pancreatin, which converts starch best in a slightly acid medium. It also tends to show how active this ferment can be, both in the stomach and upper intestine, in completing the starch digestion before the secretions become alkaline to enable the trypsin to act, furthermore, it would also indicate that, in the process of normal digestion, the food, after leaving the stomach, is in the proper stage to allow the amylopsin of the pancreatin secretion which it meets, to act quickly before the mixture is rendered distinctly alkaline to allow the trypsin to act.

These investigations have also demonstrated:

(a) That pepsin and pancreatin can be kept in the same solution, without change, if the degree of acidity be considered.

(b) That pepsin and pancreatin can be administered in such a solution, or mixed together in dry form, in all proportions, and that *the pepsin will retain its full proteolytic power and the pancreatin both its full amyolytic and tryptic activity*, which latter is developed after passing the stomach and becoming mixed with the alkaline secretions of the intestine.

(c) It is reasonable to believe that starchy digestion must take place to some extent, in the stomach, otherwise, the amyloptic ferment, ptyalin, would not be secreted at a point where it very soon mixes with another secretion, the gastric juice, which theoretically destroys it.

Action of HCl, in Varying Solutions, upon the Trypsin of Pancreatin.—These tests were made by macerating two grams pancreatin in twenty-five cubic centimeters of the acid solution for a longer period of contact. The lower strengths, 0.05 per cent. and 0.15 per cent., were not continued after four weeks as they commenced to grow fungus.

The activity of the powdered pancreatin used was tested for its proteolytic strength before and after the different periods of maceration in the dilute acid as given below, by digesting one gram dried egg albumin, dissolved in twenty cc. water, coagulated, after cooling adding dried carbonate of soda 0.12 gram

and pancreatin 0.25 gram, and digesting at a temp. of 104° F. until one cc. of the digested fluid mixed with forty cc. water upon the addition of one cc. nitric acid conc. no longer gave any precipitate, within five minutes after addition of the acid.

Pancreatin macerated in acid.	Albumin test completely digested in hrs.	1 hr.	4 hrs.	24 hrs.	7 days.	15 days.	4 wks.	10 wks.
Per cent.		Hrs.	Hrs.	Hrs.	Hrs.	Hrs.	Hrs.	Hrs.
0.05	13/4	13/4	13/4	...
0.15	13/4	13/4	2	.	13/4	...
0.25	13/4	13/4	2 1/2	.	13/4	3
0.30	13/4	4 1/2	...	4	2 1/4	3
0.35	13/4	3	3 1/4	5 1/2	6	5	3 1/2	3 1/2

DESTRUCTIVE ACTION OF ACIDS AND ALKALIES UPON THE AMYLOPSIN OF THE PANCREATIN IN WATER SOLUTION.

Acetic acid 8.00 per cent.	100 cc.
Pancreatin	2 1/2 grams
1/2 hour at 70° F.	Amylopsin completely destroyed
1/2 hour at 100° F.	Amylopsin completely destroyed

Hydrochloric acid 0.038 per cent. absolute	100 cc.
Pancreatin	2 1/2 grams
1/2 hour at 100° F.	Required 4 hours for U. S. P. test
1 hour at 100° F.	Required 12 hours for U. S. P. test
24 hours at 70° F.	Destroyed in 24 hours

Hydrochloric acid 0.095 per cent. absolute	100 cc.
Pancreatin	2 1/2 grams
1/2 hour at 70° F.	Retained full activity
1 hour at 70° F.	Retained full activity
1/2 hour at 100° F.	Completely destroyed
1 hour at 100° F.	Completely destroyed

Hydrochloric acid 0.127 per cent. absolute	100 cc.
Pancreatin	2 1/2 grams
1/2 hour at 70° F.	Nearly destroyed. Does not stand U. S. P. test after 24 hours
1/2 hour at 100° F.	Completely destroyed

Hydrochloric acid 0.38 per cent. absolute	100 cc.
Pancreatin	2 1/2 grams
20 minutes at 70° F.	Completely destroyed

Hydrochloric acid 1.90 per cent. absolute	100 cc.
Pancreatin	2 1/2 grams
	Destroyed in 2 minutes

Sodium carbonate anhydrous	0.05 gram
Water	100 cc.
Pancreatin	2 1/2 grams
1 hour at 70° F.	Retained full activity
1 hour at 100° F.	Required 1/2 hour for U. S. P. test

Sodium carbonate anhydrous	0.125 gram
Water	100 cc.
Pancreatin	2 1/2 grams
1/2 hour at 100° F.	Required 1/2 hour for U. S. P. test
1 hour at 110° F.	Required 1 1/2 hours for U. S. P. test
1 hour at 70° F.	Required 20 minutes for U. S. P. test

Sodium carbonate anhydrous	0.25 gram
Water	100 cc.
Pancreatin	2 1/2 grams
1 hour at 70° F.	Required 3/4 hour for U. S. P. test
1 hour at 100° F.	Completely destroyed

Sodium bicarbonate	0.10 gram
Water	100 cc.
Pancreatin	2 1/2 grams
1 hour at 70° F.	Retained its full activity
1 hour at 100° F.	Retained its full activity

Sodium bicarbonate	0.25 gram
Water	100 cc.
Pancreatin	2 1/2 grams
1 hour at 70° F.	Retained its full activity
1/2 hour at 100° F.	Required 1/2 hour for U. S. P. test

Sodium bicarbonate	0.50 gram
Water	100 cc.
Pancreatin	2 1/2 grams

1 hour at 70° F.	Required 3/4 hour for U. S. P. test
1 hour at 100° F.	Completely destroyed

Sodium bicarbonate	2 1/2 grams
Water	20 cc.
Pancreatin	7 1/2 grams

Kept at 100° F. for 24 hours
Amylopsin completely destroyed
Trypsin activity reduced a half

Caustic soda N/1 solution	3 cc.
Water	17 cc.
Pancreatin	0.25 gram

Destroyed trypsin and amylopsin in 15 minutes at 104° F.

Hydrochloric acid 0.05 per cent.	25 cc.
Pancreatin	2 grams

24 hours at 70° F.	Required 4 1/2 hours to stand U. S. P. test
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BROOKLYN, N. Y.,
November, 1910.

THE ASH CONTENT OF CAPSICUM.

By HARRY E. SINDALL.
Received July 25, 1911.

Since the Food and Drugs Act has become a law, Circular No. 19, Office of the Secretary of Agriculture, on the Standards of Purity for Food Products, previously published, has received an added interest and importance, since it serves as a guide to the officials in charge of the enforcement of the law, as well as to the manufactures of food products. In view of this fact, and in fairness to all concerned, it is important that these standards be stringent enough to exclude wilful adulteration or careless manufacture, and still not be too exacting to discriminate against pure products. Standards for manufactured articles are necessarily more or less arbitrary, as they must be based on honest commercial practice and custom, but standards for natural products are based on the analysis made of a great number of samples of the article in question, the more the better. The author does not intend to criticize these standards, for, as a whole, they seem fair and just, but in some instances they seem hardly possible of attainment with the natural products in the market to-day. The spice grinders in particular have had many difficulties with the total and acid-insoluble ash of capsicum or red pepper. In order to establish fair standards, it is important that all available data on undoubtedly pure samples should be published, and with this in view, the writer contributes the data tabulated below.

The first five tables represent samples of large lots of capsicum, cleaned and ground in the factory, under the personal supervision of the writer, arranged by years to show annual variations. These samples are composites taken at frequent intervals during grinding, and each one represents, as near as possible, the composition of about five hundred pounds of ground capsicum. The peppers in the first four tables contained practically no stems, while Table V is self-explanatory in this respect. The American Cayenne of Table VI was not sifted before grinding, to the knowledge of the author. In addition to the above are given analyses of ground capsicum pur-

chased in open market during the present year. Although the writer cannot vouch for the care taken in cleaning the pods before grinding, it may be said that these samples represent reputable houses only, and show the character of the better grade of ground capsicum on the Eastern market to-day. As a matter of interest are included a few analyses to show the nature of the refuse which is sifted from the pods in the millroom before grinding. The A. O. A. C. methods of analysis were used.

TABLE I.—GROUND IN 1909

Total ash. Per cent.	Acid-insolu- ble ash. Per cent.	Total ash. Per cent.	Acid-insolu- ble ash. Per cent.
5.65	0.73	6.51	1.08
5.70	0.81	6.37	0.81
5.44	0.69	6.20	0.88
5.50	0.73	6.48	1.08
5.88	0.80	6.30	0.92
5.70	0.93	6.20	0.89
5.70	0.86	6.28	0.75
6.12	0.72	6.59	0.81
6.08	0.82	7.14	0.77
6.38	0.95	7.00	0.77
Aver., 5.81	0.80	Aver., 6.50	0.87

TABLE II.—GROUND IN 1910.

Total ash. Per cent.	Acid-insolu- ble ash. Per cent.	Total ash. Per cent.	Acid-insolu- ble ash. Per cent.
6.20	0.65	6.55	0.78
6.48	0.68	6.66	0.71
6.12	0.75	6.94	0.73
6.52	0.73	6.70	0.83
6.96	0.64	6.64	0.54
6.95	0.70	6.73	0.52
6.53	0.72	6.58	0.62
6.39	0.67	6.80	0.64
6.09	0.73	8.43	0.67
7.78	0.50	7.60	0.60
Aver., 6.60	0.68	Aver., 6.96	0.66

TABLE III.—GROUND IN 1911.

Total ash. Per cent.	Acid-insolu- ble ash. Per cent.	Total ash. Per cent.	Acid-insolu- ble ash. Per cent.
5.86	0.52	6.30	0.56
5.91	0.61	6.00	0.63
6.52	0.70	5.93	0.55
5.64	0.70	5.79	0.45
6.22	0.59	5.85	0.52

TABLE IV.—SMALL AFRICAN CHILLIES. GROUND IN 1911.

Total ash. Per cent.	Acid-insolu- ble ash. Per cent.	Total ash. Per cent.	Acid-insolu- ble ash. Per cent.
8.05	2.17	6.54	0.82
7.95	2.21	6.51	0.86

TABLE V.—LARGE AFRICAN POD (ABOUT 2" LONG). GROUND IN 1911.

With stems.		Without stems.	
Total ash. Per cent.	Acid-insolu- ble ash. Per cent.	Total ash. Per cent.	Acid-insolu- ble ash. Per cent.
7.84	0.55	6.04	0.96
7.88	0.57	6.20	1.10
		6.10	0.44
		6.20	0.51

TABLE VI.—AMERICAN CAYENNE.

Total ash. Per cent.	Acid-insolu- ble ash. Per cent.	Total ash. Per cent.	Acid-insolu- ble ash. Per cent.
8.33	0.94	7.18	1.33
9.37	1.83	7.08	1.52
8.98	1.83	7.40	0.58
9.11	1.61	7.37	0.57
9.17	1.56		

TABLE VII.—COMMERCIAL SAMPLES PURCHASED IN 1911.

Total ash. Per cent.	Acid-insolu- ble ash. Per cent.	Total ash. Per cent.	Acid-insolu- ble ash. Per cent.
7.67	0.82	7.33	0.63
7.70	0.78	6.35	0.82
6.15	0.90	8.86	1.06
6.30	0.94	6.88	0.99
6.48	1.11	7.35	0.76
6.46	1.14	7.26	0.53
5.47	0.79	7.43	1.48
7.06	0.63	6.25	0.72
6.96	0.96	6.87	1.04
7.27	0.56	7.55	0.76
5.45	0.69	8.87	1.03
7.01	0.66	7.33	0.49
7.46	0.54	7.55	1.36
Aver., 6.72	0.80	Aver., 7.37	0.89

TABLE VIII.—REFUSE SIFTED FROM PODS BEFORE GRINDING

Total ash. Per cent.	Acid-insolu- ble ash. Per cent.	Total ash. Per cent.	Acid-insolu- ble ash. Per cent.
47.23	36.97	49.84	39.45
52.86	39.57	50.88	38.25

Circular No. 19 allows a maximum total ash of 6.5 per cent. and 0.5 per cent. acid-insoluble ash. The first three tables show the impossibility of keeping down to these limits, even when grinding the best grades of pods and cleaning as thoroughly as possible. The total ash requirement would exclude many pure samples, and practically none of them can be brought down to the limit of acid-insoluble ash. The tables also show that a variation may occur in the run of capsicum in different seasons. Also, as might be expected, high total ash is not necessarily caused by high acid-insoluble ash. In other words, acid-insoluble ash, being mostly in the form of adherent sand, is independent of the natural ash of the pod.

Considering the above data, taken in connection with several years' experience with this spice, it would appear that the Standards for total ash and acid-insoluble ash should be raised to 7 per cent. and 1 per cent., respectively. This can generally be obtained by careful factory practice, and would exclude dirty and carelessly ground capsicum.¹ The official Swiss standard for capsicum are 6.5 per cent. total ash and 1 per cent. insoluble ash. It should be remembered, in this connection, that capsicum or any other spice should not be condemned by the analysis of one package, as all practical spice grinders know that a large stone may get into the mill, in spite of careful cleaning. At least four packages should be analyzed separately.

LABORATORY WEIKEL & SMITH SPICE CO.,
PHILADELPHIA, PA.

ESTIMATION OF MORPHINE BY EXTRACTION WITH PHENYL-ETHYL ALCOHOL.²

By A. D. THORBURN

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Phenylethyl alcohol dissolves a little more than one-twentieth its weight of crystallized morphine

¹ Schweiz Lebensmittelbuch, 2nd Ed., p. 197.

² Read before the Pharmaceutical Section of the American Chemical Society.

alkaloid at room temperature; this alcohol is only slightly soluble in water; it seemed possible, therefore, to extract morphine alkaloid from an aqueous solution of its salt by making the solution alkaline and washing out the alkaloidal base with phenylethyl alcohol.

One difficulty in following this plan was the formation of an emulsion that separated very slowly. This emulsion formed regardless of the kind or amount of alkali used; it seemed to break down quickly when the mixture was warmed but the aqueous liquid became turbid as the mixture cooled; saturating the aqueous liquid with salt caused a slow separation—adding one-third to one-half volume of ethyl alcohol to the aqueous liquid gave a mixture that separated quickly and sharply. Benzene added to the phenylethyl alcohol interferes with the formation of this emulsion and also serves as a diluent; one volume of benzene and three volumes of phenylethyl alcohol gave satisfactory results as the extracting liquid. This floats on the water and ethyl alcohol, and even after vigorous shaking does not emulsify, but separates sharply within a few minutes.

Based on these and other experiments, the following method has been devised:

Take a quantity of the sample representing less than 0.175 gram of anhydrous morphine alkaloid; dissolve in a few cubic centimeters of faintly acid water, or if a more bulky solution is obtained, reduce on a water bath to a few cubic centimeters; cool and add three-sevenths volume of ethyl alcohol; if necessary, filter this solution into a separator, washing beaker and filter with enough 30 per cent. ethyl alcohol to make a total volume of ten to fifteen cubic centimeters; add enough stronger ammonia water to neutralize and four or five drops additional; add a mixture of phenylethyl alcohol 3 cc. and benzene 1 cc.; shake hard for several minutes, let stand and shake for several minutes again; when completely separated, draw off the aqueous liquid from the bottom of the separator into a beaker and pour the phenylethyl alcohol from the top into a second beaker. Return the aqueous liquid to the separator and repeat the extraction as before with a mixture of phenylethyl alcohol 1.5 cc. and benzene 0.5 cc., and after drawing off again extract; collect the second and third portions of phenylethyl alcohol in the beaker containing the first portion.

The alkaloidal solution in phenylethyl alcohol should be heated in a bath of boiling water for an hour; then pour the residue into a separator, washing with ether, add a few cubic centimeters at a time, until twenty cubic centimeters in all are used.

Add a known volume of tenth-normal sulphuric acid, preferably 10 cc., and shake vigorously for 5 minutes; repeat the shaking at intervals of a few minutes, keeping the acid in contact with the phenylethyl alcohol for half an hour. Draw off the clear acid aqueous liquid to a beaker. Wash the separator with 3 cc. of distilled water, shaking the mixture vigorously for several minutes and waiting for sharp

separation before drawing off. Repeat this washing three times.

Titrate back with tenth-normal potassium hydroxide; use hematoxylin as indicator. Each cubic centimeter of tenth-normal acid consumed is equal to 0.030 gram crystalline morphine alkaloid or 0.0283 gram anhydrous alkaloid; the factor to change the anhydrous alkaloid to crystalline sulphate is 1.328, or each cubic centimeter of tenth-normal acid represents 0.0376 gram crystallized morphine sulphate.

This method has been used with solutions of both commercial morphine sulphate and morphine alkaloid precipitated from the sulphate. Commercial morphine sulphate was dissolved in sufficient water so that each ten cubic centimeters contained 0.1214 gram, and by extraction with phenylethyl alcohol as described in the foregoing, 0.1218 gram was shown to be present; in 15 cc. of the same solution containing by calculation 0.1821 gram the result from extraction was 0.1789 gram crystallized sulphate.

Another sample of commercial morphine sulphate was dissolved in sufficient water so that each ten cubic centimeters contained 0.1424 gram, and the result from the extraction was 0.138 gram crystallized sulphate.

A small quantity of precipitated morphine alkaloid was dissolved in exactly 50.25 cc. tenth-normal sulphuric acid and water added to make 100 cc. Ten cubic centimeters of this solution, representing 5 cubic centimeters tenth-normal acid, required 2.07 cc. of tenth-normal potassium hydroxide to neutralize, showing 0.0838 gram anhydrous morphine alkaloid present; another trial showed 0.0852 gram. Extracting ten cubic centimeters of this solution by the foregoing method gave in two trials 0.0863 gram and 0.0869 gram anhydrous alkaloid.

Another portion of precipitated alkaloid was dissolved in the same way as before; direct titrations gave 0.0918 and 0.0915 gram present in ten cubic centimeters; and extraction with phenylethyl alcohol gave 0.0897 gram and 0.0867 gram anhydrous morphine alkaloid in ten cc.

The extraction of the alkaloid from its aqueous solution by phenylethyl alcohol and benzene should be continued until tests with Mayer's reagent or iodine show complete removal of the alkaloid from the aqueous liquid. Ordinarily this occurs with the first two extractions.

If desired, the separator can be washed with alcohol or benzene after all the alcohol has been extracted and this wash liquid added to the solution (alkaloidal) in the beaker.

The alkaloidal solution may be evaporated to constant weight. If this be done it is advisable to evaporate as quickly as possible, but not above 100° C. until a dry residue is obtained and then to constant weight at 110° C. A large proportion of the residue is crystalline but there is also an amorphous dark brown portion which is increased if the evaporation be carried on at higher temperature. The evaporation of the phenylethyl alcohol in a current of ether

vapor or of warm air was tried but did not seem to offer any pronounced advantages. The dry residue should be titrated; the results by weight constant to 110° C. are a little high. In some cases fiftieth-normal acid and alkali instead of tenth-normal may be used to advantage in the final titration.

Following the method as given, a final result has been obtained in four hours after weighing the sample to be examined. About four or five hours longer would have been required if the alkaloidal solution had been brought to a dry residue before titrating.

Sodium bicarbonate has been used instead of ammonia water, but the results were about two per cent. high, probably due to some of the alkali going through to the titration.

One objection to the method is the cost of phenylethyl alcohol: the present market price is \$2.00 per ounce or \$25.00 per pound, but since an ounce is sufficient for four or five estimations, this figure is not entirely prohibitory.

Any sample, such as powders, hypodermic tablets, compressed tablets, etc., from which a satisfactory solution can be prepared, is suitable for this method. Obviously the identity of the alkaloid is not considered, nor is a separation of morphine from other alkaloids taken into account, but as a control test for checking the manufacture of tablets, etc., the method is believed to be satisfactory.

ABSTRACT.

An aqueous solution containing morphine is made alkaline and shaken with a mixture of phenyl-ethyl alcohol and benzene; the solution of the alkaloidal in phenylethyl alcohol is then partially evaporated and titrated. The method is designed for quantities of sample representing less than 0.175 gram anhydrous alkaloid and can be completed in about 4 hours.

LABORATORY OF PITMAN-MYERS COMPANY,
INDIANAPOLIS, IND., May 18, 1911.

PLANTS AND MACHINERY

TRANSFORMING STATIONS OF NIAGARA ELECTROCHEMICAL AND ELECTROMETALLURGICAL INDUSTRIES.¹

By A. J. JONES.

Grouped around Niagara Falls are seven hydroelectric generating stations, four of which are on the Canadian side. From these seven stations energy is being used at the rate of 128,000 h. p. for electrochemical purposes, 56,000 h. p. for railway service, 36,000 h. p. for lighting, and 55,000 h. p. for various industrial services, the total being 275,000 h. p., or about 5.5 per cent. of the available power of the cataract. Of this total amount 146,000 h. p. is employed locally in industries that have been attracted to Niagara Falls by reason of the generating stations located there, electrochemical processes forming 87 per cent. of this amount and 46 per cent. of the total amount utilized.

The brief description here given of some of the installations for transforming and distributing this power in electrochemical plants, together with a discussion of the more salient features, it is hoped, may prove of interest. In any event, the rapid progress of the electrical art makes desirable a frequent comparison of notes regarding methods of design and operation.

INTERNATIONAL ACHESON GRAPHITE COMPANY.

The new 11,000-volt transformer station of the International Graphite Company, with a capacity of 2,800 kw., made up of one 1,600 kw. and three 400 kw. units, is thoroughly modern in all the details of its design.

This station is supplied with power by The Niagara Falls Power Company. Two 3/0 (85 sq. mm.), 3-conductor, lead-sheath cables, with provision for a third cable, each capable of transmitting approximately 3,200 h. p., connect this station with the step-

up transformer plant of the power company. A second station operated by the International Acheson Graphite Company receives its energy from the same power company but in the form of 2,200 volt, 2-phase power. This station is fed by two 2-phase underground feeder systems, each system being made up of four 1,000,000 cir. mil. (506 sq. mm.) lead-sheathed cables with a capacity of 2,000 h. p. per phase.

The switch room of the 11,000-volt station is situated on the west side of the International Acheson Graphite's new furnace room in a two story brick building with a floor space of approximately 21 feet by 41 feet (6.3 × 12.3 meters). On the lower floor are located the switching apparatus, bus bars, meter transformers, etc. On the second floor are located the switchboards and low-voltage control apparatus (Fig. 1).

The incoming power cables enter through a subway which extends the full length of the building. On each side of the subway are erected the masonry cells enclosing the oil circuit-breakers for both the incoming and outgoing circuits. Directly over the subway above the oil circuit breaker cells is located the bus-bar structure made of seasoned maple. Disconnecting switches mounted on porcelain insulators fastened to marble slabs are bolted to each side of the bus-bar structure. Suspended from the ceiling in line with the disconnecting switches are two platforms containing meter transformers.

Each incoming power cable terminates in a brass pot head; thence passes through current transformers to the oil switch; thence to disconnecting switches to the bus-bars.

The oil switches are of General Electric make, form K12, 15,000 volt, of 300 ampere capacity, operated from the switchboards above by link connection.

There are four switchboard panels of blue Vermont marble 7 feet 6 inches (2.25 meters) high. One panel 30 inches (0.75 meter) wide controls the three incoming

¹ Presented at the General Meeting of the American Electrochemical Society, Toronto, September, 1911.

cables. On this panel are mounted two watt-hour meters which measure the total power delivered to the bus-bars, a bracket-type voltmeter and time-limit relay of the bellows type. The other three panels are 20 inches (0.5 meter) wide and control the 1,600 kw. unit and two 400 kw. units, the third 400 kw. unit being located in a separate building with its switching apparatus in the same room with the transformer. On each of the unit panels are mounted an ammeter, indicating wattmeter, special voltmeter for indicating the position of the secondary switch, a secondary voltmeter, watt-hour meters and control switches for operation of the regulator switch.

The regulator transformers are located a short

age variation of 40 to 160 volts with full output at any voltage. Two of the 400 kw. units have a voltage range of 80 to 160 volts. The third 400 kw. unit has a secondary voltage variation of 30 to 60 volts. The regulation is accomplished by means of a dial switch which is rotated by an induction motor controlled from the switchboards in the switch room. The rotating switch of the 1,600 kw. unit consists of two dials of 22 points each mounted on a 2-inch (5 cm.) marble slab in a dust-proof case. The 400 kw. units have single dials of the same number of points as the 1,600 kw. unit (Fig. 2). As all the regulating is done on the primary side of the transformers, the volts per step are quite high. In order to have this

switch meet the heavy duty required of it, manufacturers have arranged two electrically operated switches or contactors, in series with each half of the rotating switch. These operating circuits are so connected to a small contact device on the main switch as to open auxiliary contactor and interrupt the contact and again close the circuit after it has made contact with any of the various stationary contacts. With this arrangement all arcing is removed to the auxiliary contacts which are made with heavy and easily replaceable parts.

The arrangement of the 2,200 volt station is similar to the 11,000 volt station just described. The incoming feeders enter through a manhole in the lower floor of the switch house which is situated on the west side of the graphite furnace room. The incoming power passes through General Electric K4 oil circuit-breakers, thence through knife switches to bus-bars mounted on an iron framework back of the switch-board. On the main floor of the switch house, in addition to the receiving panels, there are located two 150 kw. and two kw. oil-insulated, self-cooled, General Electric transformers with 230-volt secondaries which supply power to the motor circuits; two 17½ kw. oil-insulated, self-cooling transformers with 11-volt secondaries used for lighting, two water switches for control of the main units, one 180 kw. induction regulator and one 5 kw. motor generator set used for arc lighting and experimental work.

On the second floor of the switch house are located three switchboard panels controlling the motor and light transformers and main regulating transformer, also three low-tension panels connected to the low tension side of the motor and light transformers. The high tension panels are constructed of blue Vermont marble 24 inches (0.6 meter) wide mounted with oil circuit-breakers, ammeters, voltmeters, and watt-hour meters. The low-tension panels are equipped with knife-switches, cartridge-fuses, and 3-pole, 600-volt, carbon-break circuit-breakers.

There are two regulating transformers used for furnace operation, each with a capacity of 1,600 kw.,

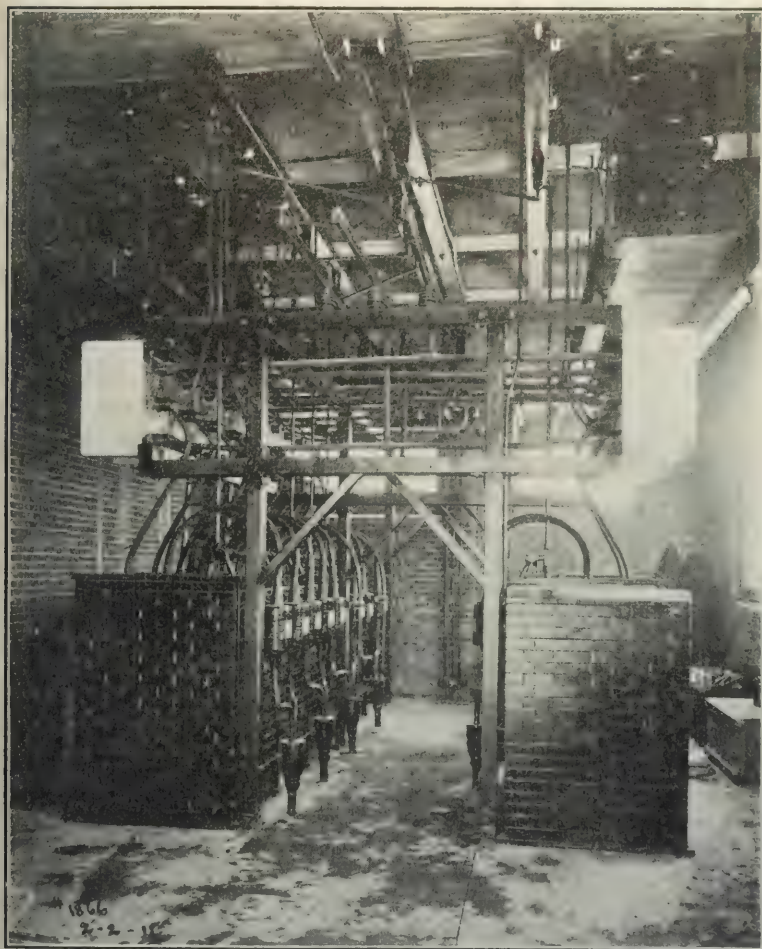


Fig. 1.

distance from the switch house in separate bays and are fed by a duplex lead-sheathed cable. The oil circuit-breakers that control the transformers are of the same type as the circuit breakers on the incoming cables except that they are 2-pole instead of 3-pole. The selector switches are single pole, double throw, so arranged that the units may be connected to any one of the three phases.

The regulators represent the latest development of the General Electric Company and are known as the transformer type of regulator. They are oil-insulated, water-cooled with primaries wound for 11,000 volts. The 1,600 kw. unit is capable of a volt-

one manufactured by the Westinghouse Electric & Manufacturing Company and the other by the General Electric Company. They are oil-insulated water-cooled. The Westinghouse unit is capable of a voltage regulation of 80 to 190 volts and is made up of a 180 kw. induction regulator in series with the primary of the main auto-transformer. Taps of the main transformer are connected to a series of oil switches which are opened and closed by drum and cam arrangement operated by a small induction motor controlled from the switch room. The main transformer gives a step by step regulation, the regulator being used to vary the voltage gradually between each step on the main transformer.

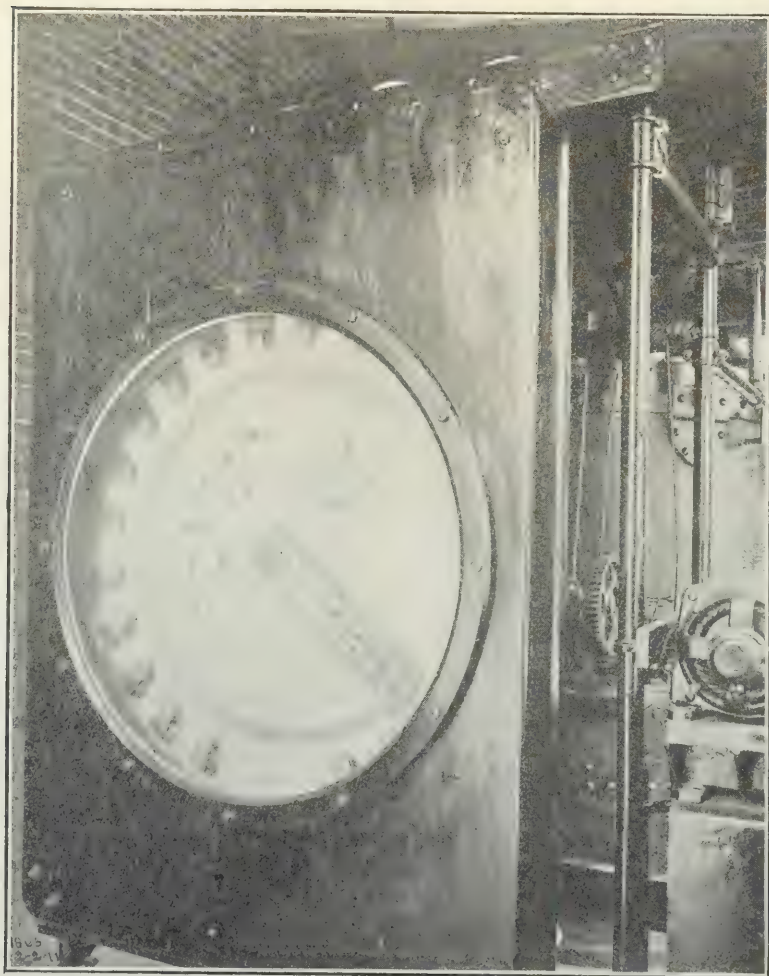


Fig. 2.

The General Electric unit (Fig. 3) is similar to the 11,000 volt units just described except that it has an additional drum-switch and is capable of giving a straight line voltage variation of 40 to 200 volts, part of this being accomplished by a motor-operated knife-switch in the secondary (Fig. 4). The accompanying diagram (Fig. 5) shows the connections of the dial switch and drum-switch (Fig. 6). The two regulating units are housed in a small brick building in the center of the furnace room. The low-tension bus-bars are constructed of aluminum and extend the full length of the furnace room.

THE ALUMINUM COMPANY OF AMERICA.

Electrical energy is supplied the Aluminum Company of America at its No. 1 Niagara Works by the Niagara Falls Power Company, delivery being made at three stations known as 1A, 6A and 10A. These stations are designated by the number of the buildings in which they are located and are of two classes, one containing rotary converters, the other regulating transformers.

The rotary converter station is of interest as being the first station to receive power from The Niagara Falls Power Company. Power was first delivered to this station in August, 1895, since which time it has been in continuous operation with very few interruptions. The equipment consists of 600 kw.

General Electric rotary converters, 2-phase, 25-cycle, running at 187.5 r. p. m., some of which are located on the west side of the station and others on the east side, the middle section of the station being occupied by banks of air-blast, step-down transformers. The transformers are single-phase with 2,200 volt primary, and are supplied with air by two blowers driven by direct-current shunt motors located on the floor of the station. A subway is carried under the transformer which conducts the air from the blowers to the transformers.

Alongside of each bank of transformers and in line with the rotary shaft is a switchboard panel which controls the primary and secondary circuit of each bank. This panel is equipped with four 2,000-volt knife-switches, without barriers, mounted at the top of the panel and four low-voltage knife-switches mounted at the bottom.

The direct current side of the rotary is controlled by a panel provided with knife-switches, field-switch and field-rheostat handle. All of the rotaries are connected on the direct current side to a bus-bar, supported on an iron framework on the west side of the station, the leads from the two rotaries on the east side being carried under the floor in a subway.

In the north end of the station are the receiving panels, two in number, one of which is equipped with single-throw, single-pole knife-switches, the other with two automatic double-pole, 1,500 ampere, type B, Westinghouse oil circuit-breakers. These panels

are made of asbestine stone and are mounted side by side on an angle framework. The incoming power cables enter through a subway and manhole under the receiving panel. They are single conductor, lead-sheathed, with a cross section of 1,000,000 cir. mils. (506 sq. mm.) each.

Transformer station 6A is located in a two-story brick building tacked on to the south wall of the carbon furnace plant. In this building are located the switchboards and control switches for six regulating transformers located in transformer houses in the furnace room. On the ground floor is an asbestine

stone panel to which are connected six 1,250,000 cir. mil. (632 sq. mm.) single conductor, paper and lead cables constituting a 2-phase and a single-phase feeder system. From the disconnecting panel the cables pass up to a marble panel on the second floor, mounted with two double-pole, remote-control, automatic, type B, Westinghouse oil circuit-breakers and necessary meters. A two-phase bus-bar system in the rear of the switchboard receives the current after it passes through the oil circuit-breakers.

In addition to the receiving panel there are five unit panels and one direct-current control panel. The unit panels are equipped with meters and oil switches, the disconnecting switches being mounted on a framework in the rear of the panels with the master switches controlling the units located in front.

The regulating transformers are located in dust-proof brick houses at distances varying from 50 to 200 feet (17 to 67 meters) from the switch house. They are known as the unit switch type of potential regulator, the electrically operated switches being of the open type, mounted on marble panels. The control voltage is 110-volt direct-current and is supplied by a small motor-generator set in the switch house.

Across the street from the carbon plant is located building No. 10, containing transformer station 10A. A small brick structure located in the center of the building houses the switchboards and transformers. The transformers are located in the basement and consist of two 1,000 kw. oil-insulated, water-cooled, General Electric transformers. One transformer is used for experimental purposes and has a range of 30 to 77 volts. The other transformer is used in conjunction with an induction regulator and is capable of giving a voltage variation of 45 to 60 volts.

The switchboard panels are located on the main floor, and consist of an incoming feeder panel and

four unit panels, one for each transformer and regulator and one for motor transformers. The receiving panel is located along the east wall of the building and is equipped with knife-switches and General Electric oil circuit-breakers. The other panels are

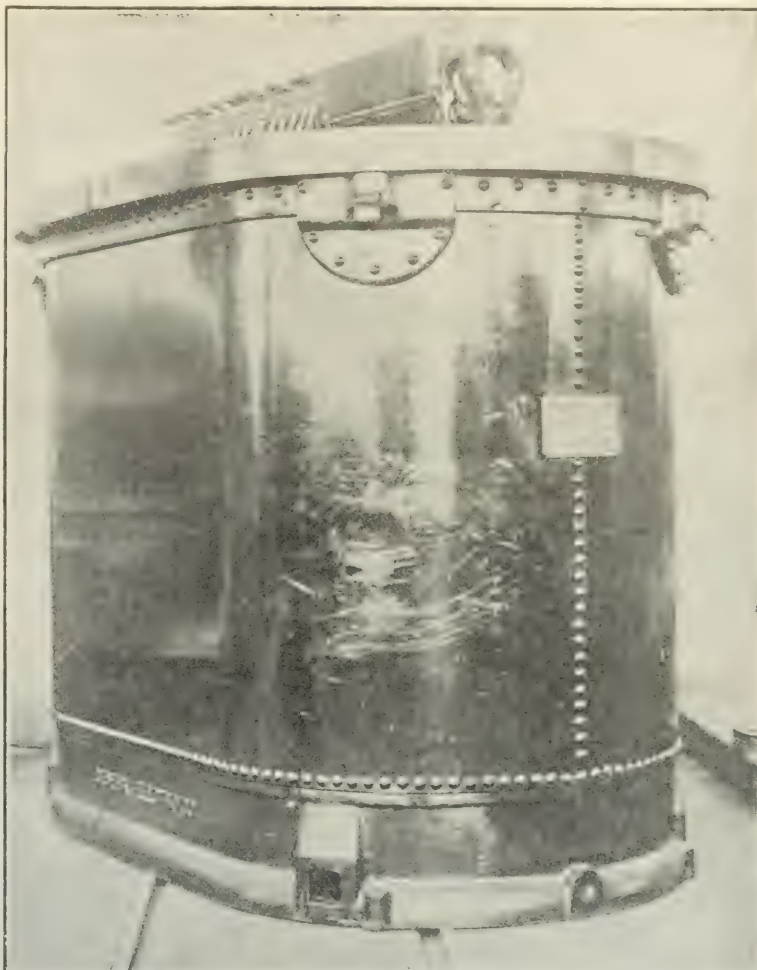


Fig. 3.

equipped with General Electric oil circuit-breakers, ammeters, and wattmeters.

A 2-phase, underground feeder system tapped to the same feeder that supplies station 6A enters the basement and connects to the receiving panel.

THE CARBORUNDUM COMPANY.

The main transformer station of the Carborundum Company is located in a rectangular brick building situated in the west end of the furnace room. In this building are located switchboards, water switches, two small motor-generator sets and two regulating transformers. Power is supplied to this station by ten single-conductor, lead-sheathed, underground cables, each having a cross section of 1,250,000 cir. mils. (632 sq. mm.) which connect to the No. 2 generating station of The Niagara Falls Power Company.

In the east end of the station facing each other are located the two regulating trans-

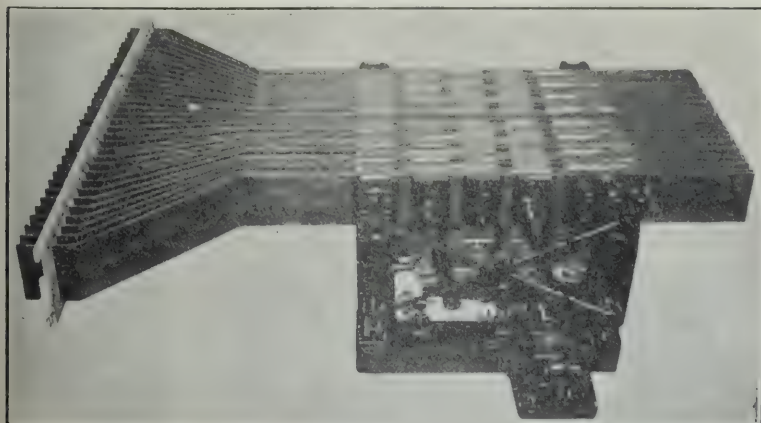


Fig. 4.

formers with their control panels. Along the south wall about four feet apart are four switchboard panels which control transformers located in bays in

from one point of the floating coil to the next. The master switches are arranged with an automatic lock to prevent their being opened too rapidly. The magnet switches themselves are so interlocked that the proper sequence of operation is insured. The main contacts are oil-immersed and entirely enclosed, making them dust-proof.

Low-voltage control cables in underground ducts connect the master switch to the regulator, the control current being supplied from the two small motor-generator sets located in the transformer house.

In addition to the regulating transformers the Carborundum Company operates two 1,500 kw. oil-insulated, water-cooled transformers with 2,200 volt primary and 100 volt secondary, manufactured by the Westinghouse Company. These units are connected to panels in the transformer room. There is no receiving panel in the station, each single-phase circuit connecting directly to a single-phase transformer panel.

Motor power is obtained from a bank of transformers located in a shed near the furnace room, consisting of four 150 kw. General Electric oil-insulated, water-cooled transformers with 440-volt secondaries.

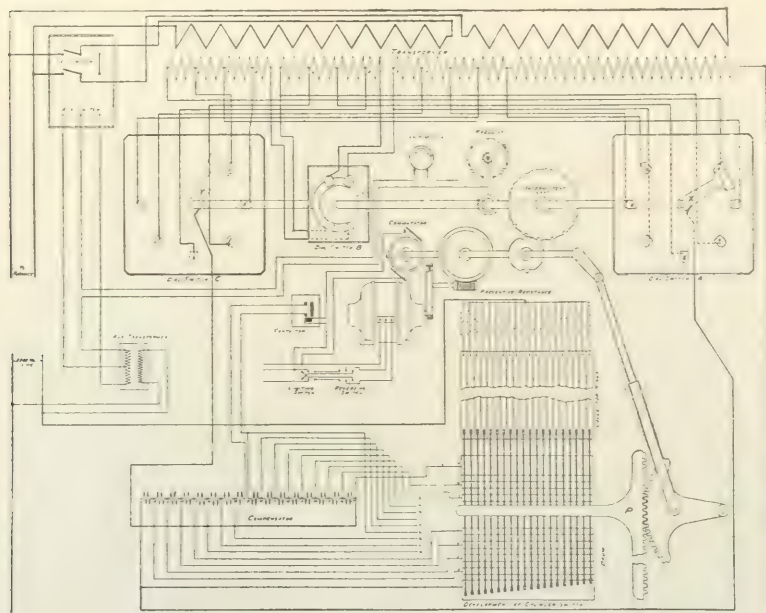


Fig. 5.

the furnace room and in the northwest corner of the station is a 2-phase motor panel.

The switchboard panels are standard single-phase panels, 24 inches wide, constructed of slate, made by the Westinghouse Electric & Manufacturing Company. Each panel is equipped with an automatic, 2-pole, type B circuit-breaker, knife-switches and meter. Above each panel on the wall are water switches consisting of an iron tank lined with a section of sewer tile 24 inches in diameter.

The regulating transformers are four in number and bear the name of the Westinghouse Electric and Manufacturing Company. They are of the oil-insulated, water-cooled type, each with a capacity of 1,600 kw., 80 to 300 volt secondary. Two of these regulators, as mentioned before, are located in the transformer station, the other two being located in transformer houses in the furnace room.

The regulators are what is known as a unit-switch type of potential regulator, being of special design for handling heavy currents. The regulator consists of a number of electrically operated switches controlled from a master switch located in front of the control panel. The transformer windings are divided into sections and two floating coils are provided which are connected to various taps on the main auto-transformer. These floating coils have intermediate steps and the successive operation of the switches connect the floating coils in proper sequence to the main auto-transformer and transfers the line connection

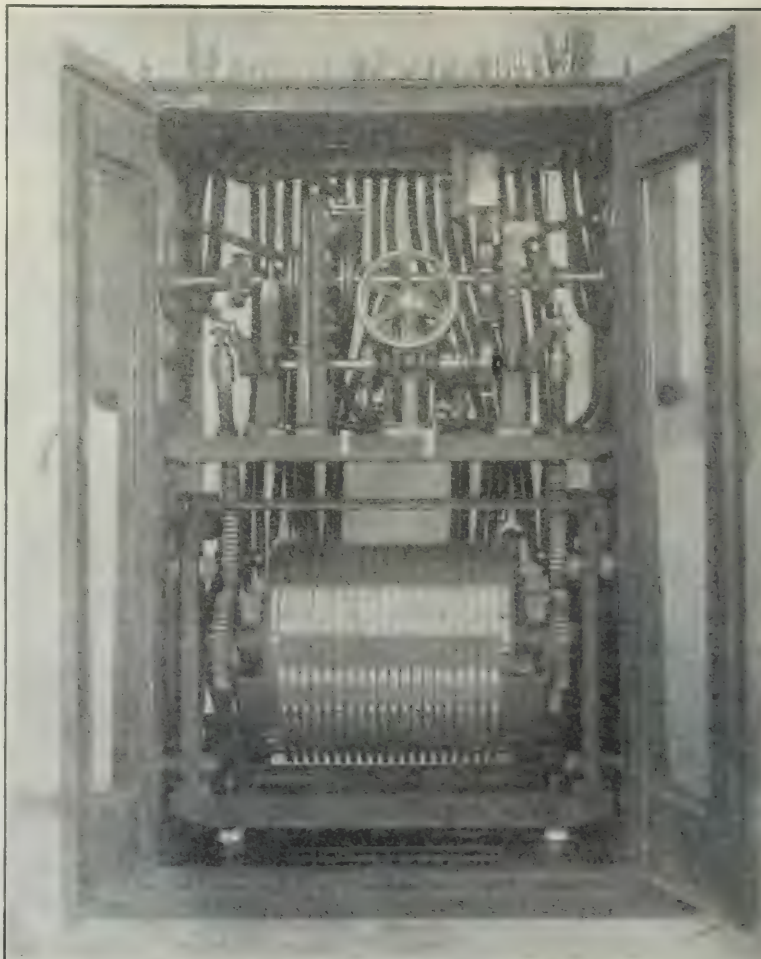


Fig. 6.

The No. 1 plant of the Carborundum Company is supplied from a small step-down transformer station in the basement of the mould building, consisting of two 150 kw. and six 50 kw. transformers, oil-insulated and self-cooled, made by the General Electric Company and one 75 kw., oil-insulated, self-cooled, Wagner transformer. The 75 kw. transformer is used for lighting, and has a ratio of 2,200 to 110,220 volts. The other transformers supply power to motors and have 440-volt secondaries. A 2-phase standard Westinghouse panel controls the incoming power, which is supplied from No. 1 generating station of The Niagara Falls Power Company by two duplex No. 2/o paper and lead cables.

NIAGARA LEAD COMPANY.

The transformer station of the Niagara Lead Company, situated in the south end of the main building, is supplied with power by The Niagara Falls Power Company by a 2-phase, 2,200 volt underground feeder system, consisting of two 3/o duplex paper and lead cables.

The incoming cables connect to a receiving panel mounted with four disconnecting switches and two 2-pole, automatic Westinghouse type B circuit-breakers. From the receiving panel the power is carried to the motors and transformers by conductors mounted on the walls on porcelain insulators.

Direct current power is obtained from two Westinghouse motor-generator sets, each consisting of a

motor belted to an overhead line shaft, which supplies the main shop with mechanical power. This motor is protected by a panel mounted with General Electric expulsion-type fuses.

On the west wall of the station are mounted two

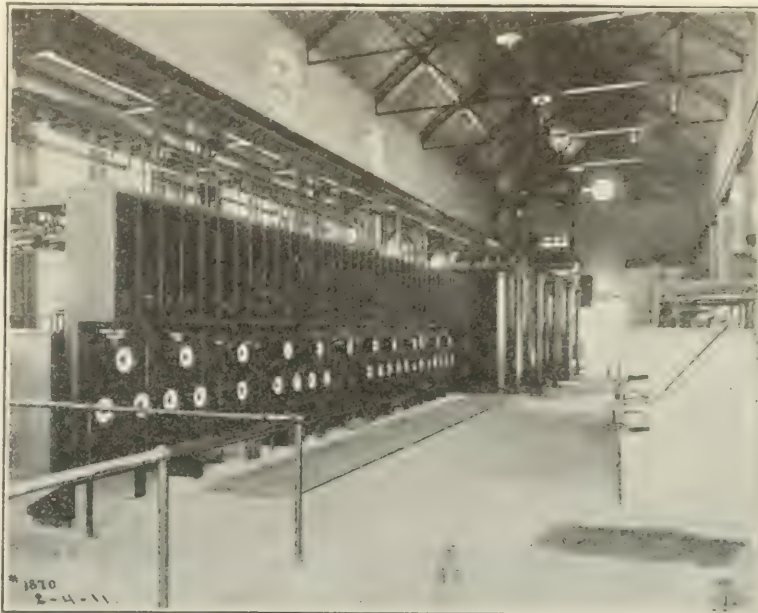


Fig. 7.

kw., oil-insulated, self-cooled, and four 5 kw., air-cooled, Westinghouse transformers, with 110-volt secondaries used for lighting. These transformers are also protected by General Electric expulsion fuses.

Each motor-generator set is provided with a motor and generator panel. The panel controlling the motor is located on the east side of the station between the wall and induction motor; ammeters, an oil-switch, auto-starter, and 4-pole, air-break circuit-breakers are mounted on the panel.

The direct current panels are located on the opposite side of the room near the west wall. Each panel is equipped with meters, field-rheostat handle, knife-switches and circuit-breakers. The direct-current power is carried to the cell-room by underground cables.

CASTNER ELECTROLYTIC ALKALI COMPANY.

Power in the form of 2-phase, 2,200-volt, 25-cycle current is delivered to the Castner Electrolytic Alkali Company at three stations located in their Niagara Falls plants.

Transformer Station No. 1 has a capacity of 1,375 kw. made up of eleven 125 kw. Westinghouse rotary converters, 500 r. p. m., 2-phase, 25-cycle, with Wagner step-down, air-blast transformers, each with a capacity

of 100 kw. These transformers have a secondary regulation of 30 volts, accomplished by means of a dial switch regulator in the primary circuit. The transformers are single-phase and are connected two in a bank to each rotary. The station is rectangular

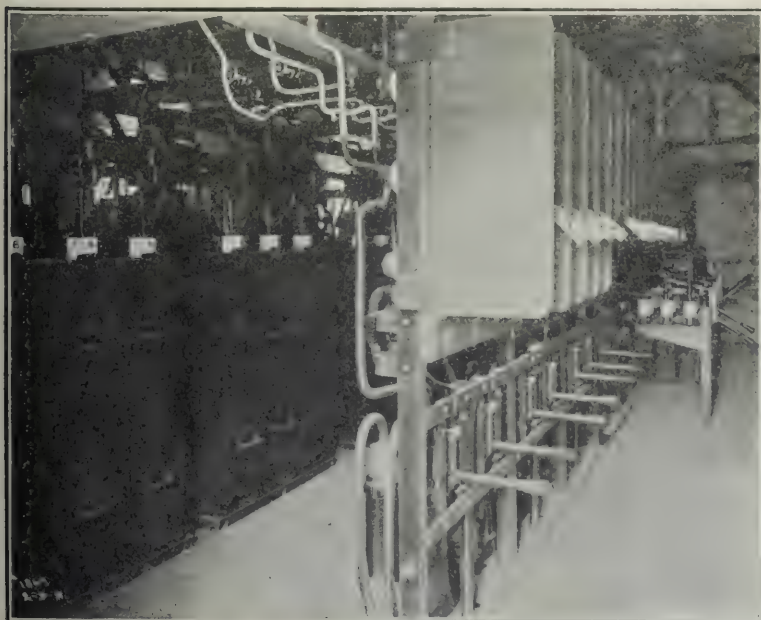


Fig. 8.

300 h. p., 2-phase, 2,200 volt, 487 r. p. m., induction motor, direct-current to a 187.5 kw., 125-volt, compound-wound, direct-current generator. In addition to the motor generator sets the station contains a 60 h. p., 2-phase, 2,200-volt Westinghouse induction

in shape with the rotary converters occupying the south side and the transformers the north side. The switchboard arrangements consist of single panels mounted opposite each unit between the transformers and rotary converters. The panels are made of white

the switchboard are both alternating and direct-current bus-bars. Located in the northwest corner of the station is the main-line panel, equipped with eight knife-switches and carbon-break circuit-breakers. The incoming cables, eight in number, have a cross section of 1,000,000 cir. mils. (506 sq. mm.) each and are capable of transmitting approximately 8,000 h. p.

Motor power for the No. 2 station is obtained from six 50-kw. Wagner transformers with 2,200-volt primary and 220-volt secondary. A 75-kw., oil-insulated, self-cooled, Wagner transformer supplies power for lighting. These transformers are controlled from a panel equipped with oil circuit-breakers.

No. 3 station of the Castner Company is equipped with an 800-kw. General Electric, oil-insulated, water-cooled transformer with 2,200-volt primary and 144-volt secondary. Connected in the secondary circuit is a potential regulator capable of varying the voltage from 85 to 225 volts. The regulator is oil-insulated, water-cooled, and of same make as the transformer. A single-phase slate switchboard is mounted in the station in front of the transformer. The switch-

board is equipped with knife-switches, oil circuit-breakers, indicating meters and watt-hour meters. The primary circuit is opened and closed through a water-switch, mounted on the wall above the transformer.

marble equipped with plug-type switches and fuse-blocks. A dial-switch with glass cover is mounted on the lower part of the panel.

In the east end of the station is located a receiving panel to which is connected eight single-conductor, lead-sheathed cables. The receiving panel is equipped with knife-switches and carbon-break circuit-breakers. There are no low-tension switchboards in the station, the direct current power being carried directly from the rotary converters to the cell room. In addition to the rotary converters the station contains four 25 kw., oil-insulated, self-cooled, Westinghouse transformers with 220-volt secondaries, which supply power to motors.

Transformer Station No. 2 has a capacity of 4,000 kw., consisting of eight 500-kw. Stanley synchronous-motor, direct-current generator sets, the motors being 2-phase, 2,200 volts and rated at 580 kw. The sets are arranged four in a row on each side of the transformer room. On opposite sides of the room, between the wall and motor-generator sets, are two eight-panel marble switchboards made by the Stanley Manufacturing Company. Each switchboard consists of four alternating-current panels and four direct-current panels, mounted side by side. The alternating-current panels are equipped with oil circuit-breakers, Stanley hot-wire ammeters and field ammeters. The direct-current panel is equipped with Weston ammeter, voltmeter, knife-switches, and circuit-breakers. Supported on brackets in the rear of



Fig. 9.

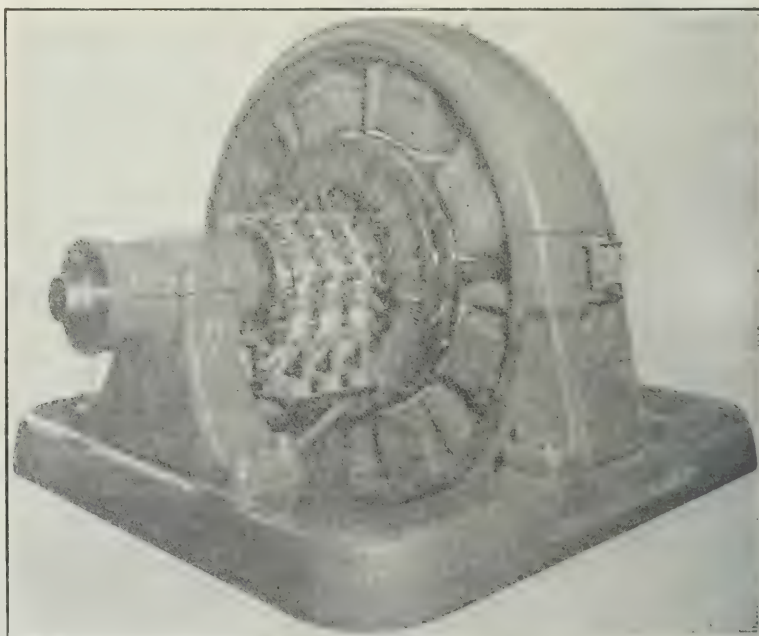


Fig. 10.

THE NORTON COMPANY.

The electrical equipment of the Norton Company at its Niagara Falls, N. Y., works is typical of the equipment of several plants in the Niagara district. Power is received at a switch house from which it is

distributed to step-down transformers located in bays along the side of the furnace room.

In the switch house are located a marble receiving panel mounted with disconnecting switches, two double-pole, General Electric, K₃, oil circuit-breakers, a motor and light panel equipped with knife-switches and General Electric expulsion fuses, and a transformer panel. Adjacent to the switch house is a transformer bay containing a 1,500-kw., oil-insulated, water-cooled, Wagner transformer with 2,200-4,400-volt primary and 110-220-volt secondary, with a water-switch mounted on the wall above the transformer. The panel for this transformer is located in the switch house.

Attached to the furnace room on the same side as the switch house are two bays containing 750-kw. units, together with control panels and water-switches. One of these transformers bears a Westinghouse name plate, the other a General Electric. Both units have a ratio of 2,200 to 110 volts, and are of the oil-insulated, water-cooled type. The bays are connected to the switch house by a pair of single-conductor, lead-sheathed cables with taps at each bay.

In the north end of the main building are located the lighting and motor transformers, consisting of two 30-kw. and two 10-kw., oil-insulated, self-cooled, Westinghouse transformers with 110- and 440-volt secondaries.

Power is supplied to the Norton Company from No. 2 generating station of The Niagara Falls Power Company by a two-phase, 2,200-volt feeder system, consisting of two 500,000 cir. mil. (253 sq. mm.) and two 1,000,000 cir. mil. (506 sq. mm.) lead-sheathed

UNION CARBIDE COMPANY.

The plant of the Union Carbide Company at Niagara Falls, N. Y., is of interest both on account of its size and on account of the great amount of power transformed by it for electrochemical purposes.

Power is distributed to the Union Carbide Company

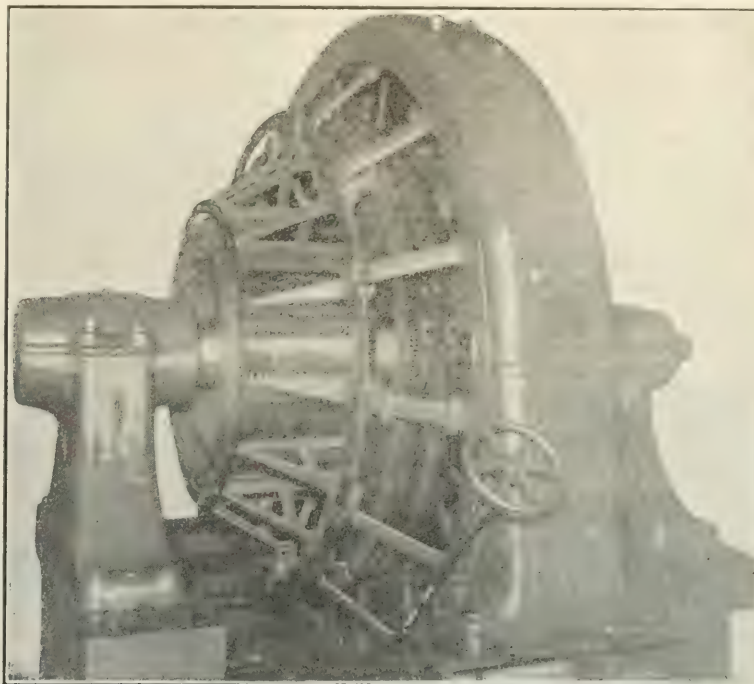


Fig. 11.

by The Niagara Falls Power Company and by the Cliff Electrical Distributing Company, from sub-stations located near the Carbide Works.

The Union Street sub-station of The Niagara Falls Power Company is located on the west side of the Carbide Company's No. 1 plant at a distance of about 60 feet. This station is used as a switching station and as a step-down station, being equipped with switch-board panels, oil circuit-breakers, and step-down transformers (Fig. 7).

The sub-station of the Cliff Electrical Distributing Company is located midway between the No. 1 and No. 2 plants and contains switching apparatus only.

In the plants of the Carbide Company, widely separated from the sub-stations, are the large low-voltage step-down transformers which supply power to the furnaces. Some of the transformers have 2,200-volt primaries and others 11,000-volt primaries. They are all of the oil-insulated, water-cooled type, the cooling water being procured from city mains.

Practically all of the 11,000-volt units have a double source of supply for their power. Bricked in the wall of the transformer bay is a marble slab mounted with a double-throw knife-switch, the middle point of which is connected to the transformer, the jaws of one side

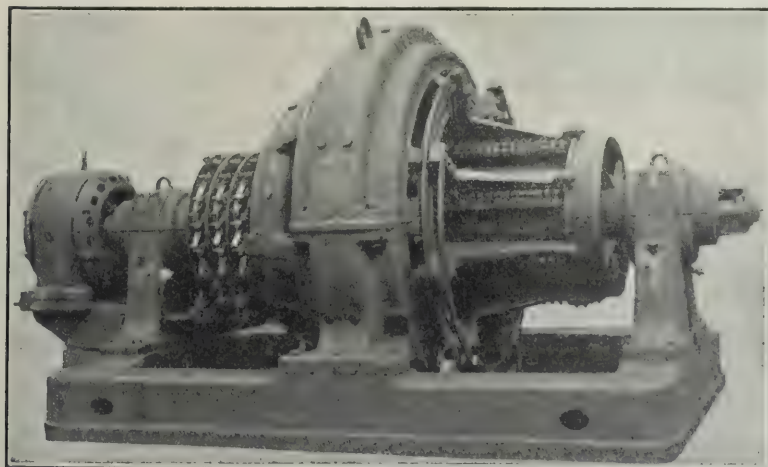


Fig. 12.

cables. The secondary current of the three furnace units is carried to the furnace room by copper bus-bars interlaced up to the furnaces. Each furnace is equipped with an indicating ammeter mounted on the wall opposite the furnace.

being connected to The Niagara Falls Power Company's circuits and those on the other side to the Cliff Electric Distributing Company's circuits.

The Union Street sub-station of The Niagara Falls Power Company has a capacity of 52,000 h. p., made up of four 1,870-kw. step-down General Electric transformers, two 11,000-volt switchboards, and one 2,000-volt switchboard, and supplies power to all of the plants in the immediate vicinity, including that of Union Carbide Company. Power is delivered to the station by eleven 3/0, 3-conductor, paper and lead cables, and a 3-phase, 500,000 cir. mil. (253 sq. mm.) aluminum overhead transmission line, both of which feed into a double bus-bar system through panels mounted with double-throw selector switches.

The switching apparatus which controls the carbide units is of two kinds: 2,000-volt and 11,000-volt apparatus. The 11,000-volt units are fed from panels equipped with ammeters, switch-handles, and double-

automatic, oil, circuit-breakers. From the knife-switches the circuits pass through the oil-switches to knife-switches and thence to bus-bars mounted on a maple framework.

The outgoing cables are connected to the bus-bars through knife-switches and non-automatic oil circuit-breakers.

NIAGARA ALKALI COMPANY.

The new transformer station (Fig. 9) of the Niagara Alkali Company will have, when completed, a capacity of approximately 1,500 kw., made up of two 705-kw., rotary converters, 6-phase, 375 r. p. m., direct-current voltage, 205 to 235 volts—one manufactured by the General Electric Company (Figs. 10 and 11) and the other by the Westinghouse Electric and Manufacturing Company (Fig. 12). The General Electric unit is known as a regulating-pole rotary converter, the direct-current voltage being varied by changing the excitation of the auxiliary poles. The Westinghouse unit regu-

lates the direct-current voltage by a synchronous regulator mounted on the same shaft as the rotary converter, and connected between the armature-windings and collector-rings. Both these rotary converters have high synchronizing power and will not drop out of step when the alternating current voltage is dropped to 40 per cent. of normal.

Power is received over a 3/0, 3-conductor, 11,000-volt, paper and lead-covered cable from the Union Street sub-station of The Niagara Falls Power Company, and stepped down in 3-phase, 870-kw., oil-insulated, water-cooled transformers to a voltage suitable for the rotary converters.

The high-tension switching apparatus consists of four 3-phase, automatic, K4, 15,000-volt General Electric oil circuit-breakers, mounted in cells, constructed of pressed brick ranged along the west wall of the transformer station. One switch controls the main-line, the other three are unit switches for control of the two rotary converters and a bank of

motor and light transformers. Above the oil switch cells is an iron-pipe structure carrying the bus-bars, meter-transformers and disconnecting-switches. The bus-bars consist of heavy insulated rubber and cambric cables, mounted on petticoat insulators. Switch-handles for operating the oil-switches are mounted on the side walls of the brick cells. A main-line disconnecting panel is fastened to the wall directly above a man-hole in the northwest corner of the station. Between the rotary converters and transformers are two starting panels mounted with 3-pole, double-throw knife-switches. On the east side of the room is a low-tension switchboard consisting of slate panels 24 inches wide. Two panels control the direct-current side of the rotary converters, and are equipped with knife-switches, circuit-breakers, indicating-voltmeter and ammeters. The other panels contain the high-tension indicating-meters and watt-hour-meters.

In addition to the rotary converters the station

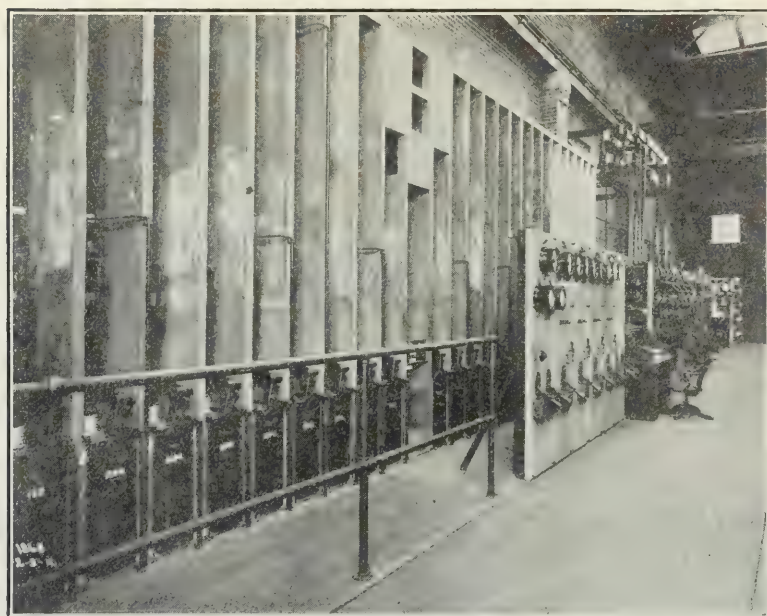


Fig. 13.

throw, single-pole knife-switches mounted on electrode insulators. The brick cells containing 2-pole, General Electric, K4, oil-switches are mounted back of the panels along the wall. Each unit is connected to the station by a duplex paper and lead cable laid in underground ducts.

The 2,000-volt units are fed from a switchboard on the east side of the station. Each unit is connected to a single-phase panel mounted with ammeters, oil circuit-breakers and selector-switches.

The sub-station of the Cliff Electrical Distributing Company consists of a one-story brick building with basement. Power enters the station at a pressure of 12,000 volts over five 3-conductor, paper and lead cables through ducts at the South end of basement (Fig. 8).

Each cable terminates in a pot-head, thence passes up to the main floor to knife-switches mounted in compartments in the rear of type C, Westinghouse-

will contain two 25-kw. and two 50-kw., oil-insulated, self-cooled, General Electric transformers with a ratio of 11,000 to 460 volts, for motor power, and a lighting transformer of 15-kw. capacity, oil-insulated, self-cooled, made by the General Electric Company, with a secondary voltage of 115 to 230 volts. All the low-tension wiring is carried underground in fiber conduit. An overhead crane of 10 tons' capacity serves the station. A pit is excavated in the north-west corner of the station, so that transformers can be readily dismantled and repaired.

HOOKEE ELECTROCHEMICAL COMPANY.

The power station of the Hooker Electrochemical Company, recently reconstructed and enlarged, presents a good example of concrete construction as applied to switchboard work (Fig. 13). The station is located in a brick building with a basement floor. Power enters the building in the form of 3-phase, 11,000-volt, 25-cycle current, over two 3-conductor, 3/0 lead-sheath, paper-insulated cables which separate into six single-conductor cables in the basement and thence pass up through the floor to disconnecting switches mounted in concrete cells on the main floor. On the south wall of the building is located the concrete structure which contains the oil-switches and bus-bars. The cells containing the Westinghouse type E oil-switches are built on the floor. Above them are the disconnecting-switch and bus-bar compartments, the latter running lengthwise of the room. The bus-bars consist of bear wire, 4/0 in cross section, mounted on petticoat insulators. The oil switches are remote-control, hand-operated, 300-ampere capacity. The high-tension switchboard panels, six in number, are of blue Vermont marble and are equipped with power-factor meters, ammeters, and switch-handles. All the meter-transformers are mounted in concrete cells, the low-tension circuits of these transformers being carried to the switchboards in iron conduits.

The 11,000-volt current is stepped down by 300 and 400 kw. oil-insulated, water-cooled, single-phase Westinghouse transformers, located in a bay on the north side of the station. The 300-kw. transformers have a ratio of 11,000 volts to 198 volts and are connected in *delta*, supplying power to rotary converters. Some of the 300-kw. transformers are arranged for 3-phase to 2-phase transformation and have a secondary voltage of 2,200 volts. The 400-kw. transformers have a secondary voltage of 220 volts, and are used for lighting and motor power.

Direct-current power is obtained from Westinghouse booster-type rotary converters (Fig. 14), 6-phase, 375 r. p. m., direct-current voltage 230 to 320; and from Burke Electric motor-generator sets consisting of 720 h. p. synchronous motors, 2-phase, 2,200-volt, 375 r. p. m., direct connected to 500-kw., 250-volt, direct-current generators, and 360 h. p., 2-phase, 2,200-volt synchronous motors, direct connected to

250-kw., 125-volt, 500 r. p. m., direct-current generators. The synchronous motors are excited by two Burke Electric exciter sets consisting of a 90 h. p. induction-motor, 2-phase, 2,200-volt, direct connected to a 60-kw., 125-volt, 720 r. p. m., direct-current generator. All the machines in the station are arranged so that they can be operated in multiple on the direct-current side, a direct-current bus-bar being carried along the rear of the low-tension switchboard. Each machine is controlled by a low-tension panel which is equipped with circuit-breakers, knife-switches and ammeters. The Burke Electric machines are controlled on the 2,200-volt side by panels equipped with oil-switches.

The low-tension circuits of the motor and light-transformers are carried to six panels mounted with four-pole knife-switches and cartridge fuses. A 2,200-volt receiving panel through which power was formerly supplied to the Burke machines is still in service, being used as a spare. The rotary converters are

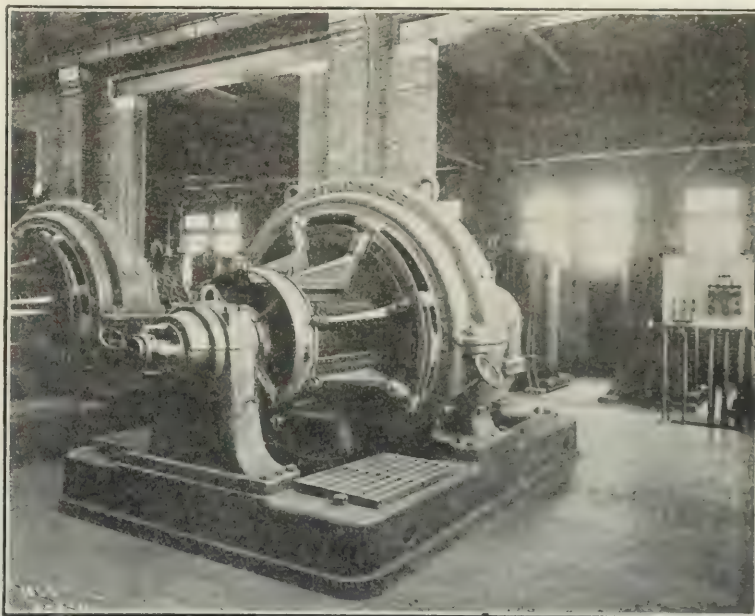


Fig. 14

synchronized by small induction-motors mounted on the end of the shaft. A low-tension starting panel, mounted with two 3-pole knife-switches, is connected in the circuit between the transformers and alternating-current side of the converters. All of the 11,000-volt apparatus was furnished and installed by the Westinghouse Electric and Manufacturing Company.

NIAGARA ELECTRO-CHEMICAL COMPANY.

The transformer station of the Niagara Electro-Chemical Company is of interest in that it contains several different types of apparatus, each of which performs the same service, but in a slightly different manner.

The function of the station is to change the 2-phase, 2,200-volt, 25-cycle current received from The Niagara Falls Power Company into direct-current power. To perform this transformation the station is equipped with three different types of apparatus, namely, rotary converters with regulating transformers, in-

duction motor-generator sets, and synchronous motor-generator sets.

The transformer station is a large roomy brick building situated on the east side of the cell room. The general scheme carried out in the station is that of locating the transformer units on the center line

panel on both the low-tension and high-tension side. The induction-motor-generator sets are of standard design made by the Westinghouse Company. Each set is connected to two marble panels mounted with the usual instruments and switches.

The synchronous-motor-generator sets are made up of three units, two direct-current generators connected to opposite ends of a synchronous-motor. Each machine is connected to a separate panel mounted with meters and circuit-breakers. The switch-board is of blue Vermont marble, designed and installed by the Westinghouse Electric and Manufacturing Company.

THE UNITED STATES LIGHT AND HEATING COMPANY.

Located in the north end of the City of Niagara Falls is The United States Light and Heating Company, which has just completed a new transformer station designed by Dodge, Day & Zimmerman, of Philadelphia. When completed the station will contain four 750-kw. rotary converters, with necessary step-down transformers; two sets have already been installed (Fig. 15).

At the present time power is received from the Cliff Electrical Distributing Company by an overhead transmission line which will soon be replaced by an underground cable system. Power enters the station in the form of 3-phase, 25-cycle current, at a pressure of 12,000 volts, and passes through General Electric disconnecting-switches mounted on insulators on a pipe framework adjoining the south

of the building with the switchboards along the walls, the receiving panels being located along the east wall and the unit panels along the west wall.

Power is delivered to the station by two 2-phase, underground feeder systems, one of which connects to a receiving panel in the south end of the station and the other to a panel in the north end of the station. A third feeder enters the building and connects to both panels. This feeder is considered a spare feeder and is used only in times of trouble on one of the other feeders. The panel in the south end receives its power from No. 1 generating station over four cables with a cross section of 1,000,000 cir. mils. (506 sq. mm.) each. The north end panel is supplied from No. 2 generating station, the cables having a cross section of 1,250,000 cir. mil. (633 sq. mm.)

Both of the receiving panels are of marble, and are equipped with eight knife-switches, single-throw, single-pole, and two double-pole Westinghouse type B, automatic circuit-breakers. From the receiving panels the power is carried to the unit panels through underground ducts in the floor of the station. The rotary converters in the south end of the station are equipped with starting motors and polyphase Stillwell regulators in the primary of the transformer circuits. The static transformers are of the oil-insulated, self-cooled type, both rotary converters and transformers being made by the Westinghouse Company. Each rotary is connected to a marble

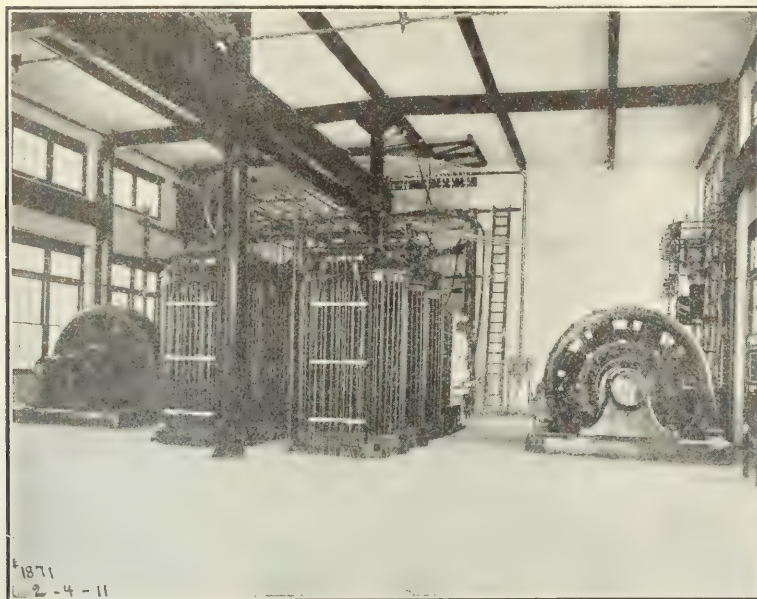


Fig. 15.

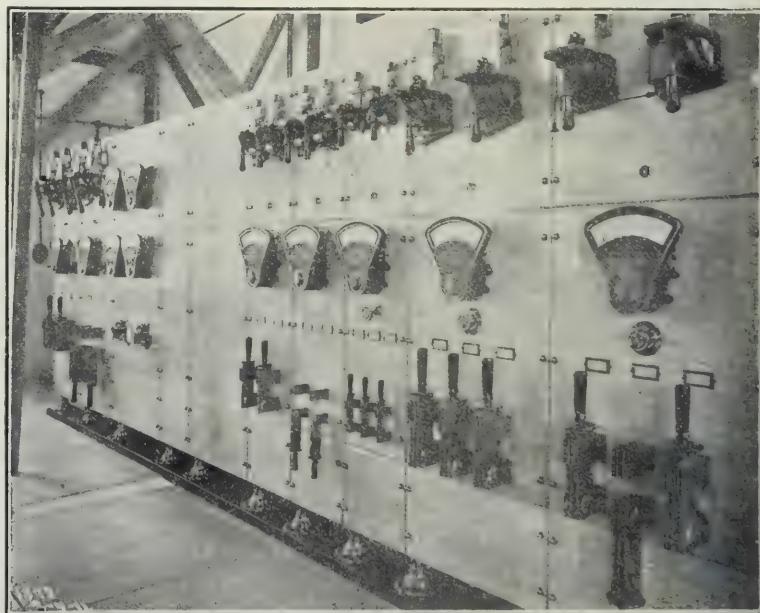


Fig. 16.

wall of the station. On each side of this iron structure are mounted meter-transformers and fuses. From the disconnecting switches circuits are carried overhead to choke-coils located on a pipe framework

mounted on top of a 3-pole, cell-type, K-12, General Electric, 15,000-volt, oil circuit-breaker. From this support the circuits pass through the oil-switch to a bus-bar system mounted directly over the static

primaries, Y-connected, and 199-volt secondaries, step-down the current for use in the rotary converters. The secondary leads of the transformers are carried to the starting panels, thence to the rotary converters through underground trenches on single-conductor, lead-covered cables.

The 750-kw., 6-phase, split-pole, 375 r. p. m., General Electric rotary converters with a direct-current voltage of 225 to 275 volts occupy space on each side of the station. The main and auxiliary field rheostats are mounted on angle iron framework near the rotary converters. Direct-current power from the rotary converters is carried to a switchboard in the east end of the station through underground ducts by single-conductor lead-covered cables.

The direct-current switchboard (Fig. 16) consists of ten blue Vermont marble panels $2\frac{1}{2}$ inches (6.2 cm.) thick, made by the Fort Wayne Electric Works. On the left-hand end, facing the switchboard, are two 30-inch (75 cm.) panels which control the direct-current side of the two rotary converters, each panel being equipped with two carbon-break circuit-breakers, two single-pole, single-throw, 5,000-ampere knife-switches, and a 6,000-ampere Thompson astatic am-

meter. Next to the rotary panel is a 36-inch (90 cm.) panel equipped with three 300-volt Thompson astatic voltmeters, one 10,000-ampere ammeter and two Sangamo watt-hour meters. Two vacant panels come next, one 18 inches (45 cm.) wide and the other

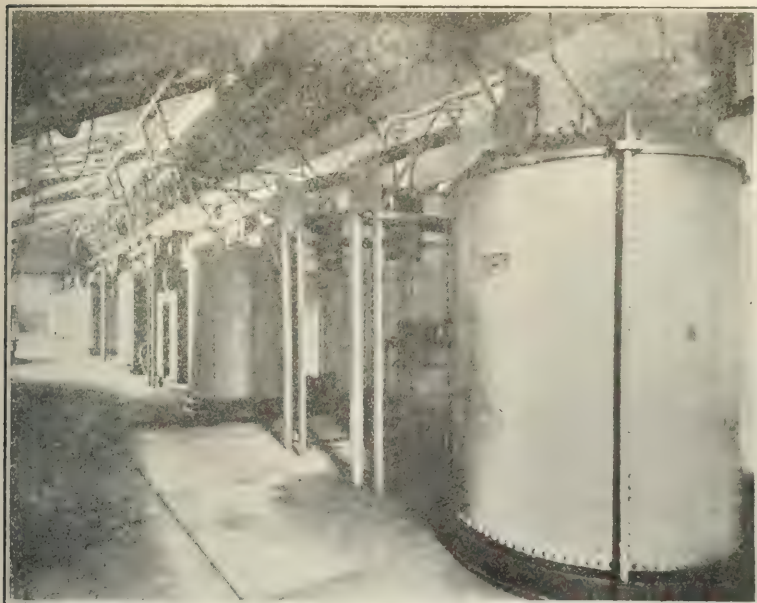


Fig. 17.

transformers supported on insulators on an iron framework.

In front of the K-12, oil circuit-breaker stands a blue Vermont marble panel equipped with Thompson horizontal-type ammeter, watt-meter, power-factor meter, time-limit relay, and switch-handle. General Electric meter-transformers are mounted on the framework above the oil-switch cells.

In the rear and at right angles to the main oil-switch structure facing in opposite directions, are two additional brick structures containing automatic, remote, control, 3-pole, 15,000-volt, K4, General Electric oil-switches, which control the primary circuits of the static transformers. Above each cell is a pipe framework on which is mounted meter-transformers.

From the main-line oil-switch the current divides and passes through each of the two oil-switches described above to the primaries of the two banks of transformers. Located in front of the switch-cells are three marble panels, one of which controls the oil-switch, another being a starting panel for a rotary converter, while the third has mounted upon it the neutral circuit-breakers. On the oil-switch panel are mounted Thompson voltmeter, ammeter, power-factor-indicator, time-limit relay and switch handle. On the starting panel are mounted a 2,500-ampere, 3-pole, double-throw knife-switch, and a 1200-ampere, 3-pole, double-throw, knife-switch. On the rear of this panel is mounted a 3-pole, carbon-break circuit-breaker in the middle point of the secondary winding of the transformers.

Two banks of transformers, each bank consisting of three 275-kw., single-phase, oil-insulated, self-cooled, General Electric transformers, with 6,930-volt



Fig. 18.

30 inches (75 cm.) wide, which have been reserved for booster controlling switch and instruments. A motor panel occupies the space beside the vacant 30-inch (75 cm.) panel. This panel is 18 inches (45 cm.) wide, and is mounted with two knife-switches, 1,500-ampere ammeters and two carbon-break circuit-

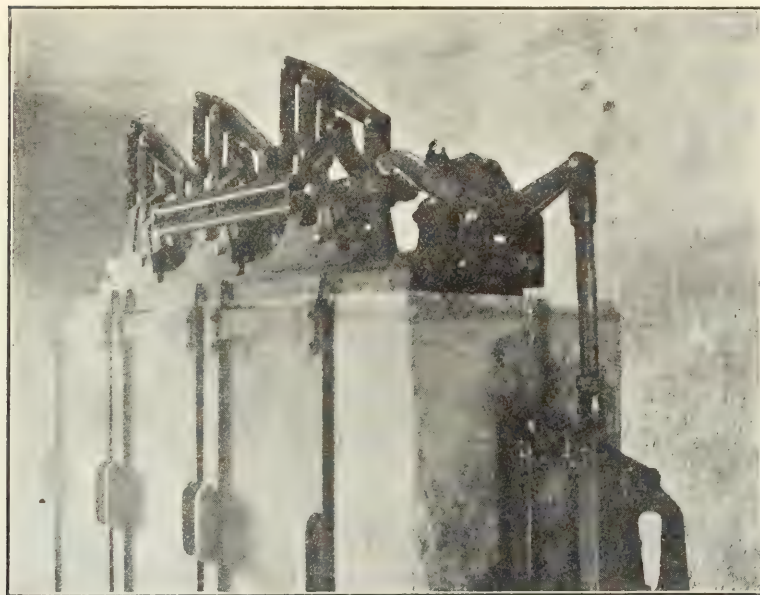


Fig. 19.

breakers. An 18-inch (45 cm.) fire-pump panel joins the motor panel, equipped with an 800-ampere ammeter, two single-pole, single-throw knife-switches and two carbon-break circuit-breakers. The eighth panel is an 18-inch (45 cm.) lighting panel, equipped with a 600-ampere ammeter, 2-pole circuit-breaker and a 3-pole, single-throw, 400-ampere knife-switch. The ninth and tenth panels are what is known as battery panels. These are each equipped with one 3,000-ampere ammeter, one 2-pole circuit-breaker and three 3,000-ampere, single-pole, single-throw knife-switches.

In the rear of the switchboard are located the copper bus-bars, three in number, constructed of 10 by $\frac{1}{4}$ inch (25×0.62 cm.) copper bars. Three bus-bars are required, as the plant is operated on a three-wire system. From this switchboard the power is carried to the shops by insulated copper cables supported on an overhead pole line. The station is served by two overhead cranes of sufficient capacity to handle any unit in the station.

ELECTRO METALS COMPANY.

At Welland, Ontario, the Electric Metals Company has installed a modern transformer station which steps-down the high voltage current received from Niagara Falls to a low voltage suitable for furnace operation.

Power is received from Niagara Falls over two pole lines, each carrying two 3-conductor transmission lines which are dead-ended at a switch platform located

in the street outside of the Electro Metals Company's plant. From this structure the current is conducted into the plant over a single-pole line carrying two 3-conductor circuits which enter a brick switch room through porcelain tubes fastened in the wall and connect to knife-switches mounted directly inside on the wall. From the knife-switches the circuits are carried to bus-bars, thence through choke-coils to a 3-pole, type H, 13,000-volt Canadian General Electric Company oil circuit-breaker, mounted in a concrete cell on the main floor.

Mounted on the east wall is a meter panel containing three Westinghouse type F ammeters, watt-hour meters, and a Westinghouse graphic wattmeter. On the floor to the left of the meter board is a concrete structure containing the meter potential transformers and fuses. Westinghouse electrolytic lightning arresters protect the incoming lines.

From the bottom of the oil-switch the circuits pass along the west wall of the switch-house to the main transformer room, where they connect to bus-bars supported on three concrete shelves built in the wall above the transformers. On a shelf on the west wall of the switch-house are three 25-kw. Packard oil-insulated, self-cooled transformers with a ratio of 12,000 to 220 volts, which supply power to the motor circuits. These transformers are protected by a General Electric 3-pole, K-4, oil circuit-breaker (Fig. 17).

In the main transformer room are located seven 750-kw. units with 12,000-volt primaries and 40-volt

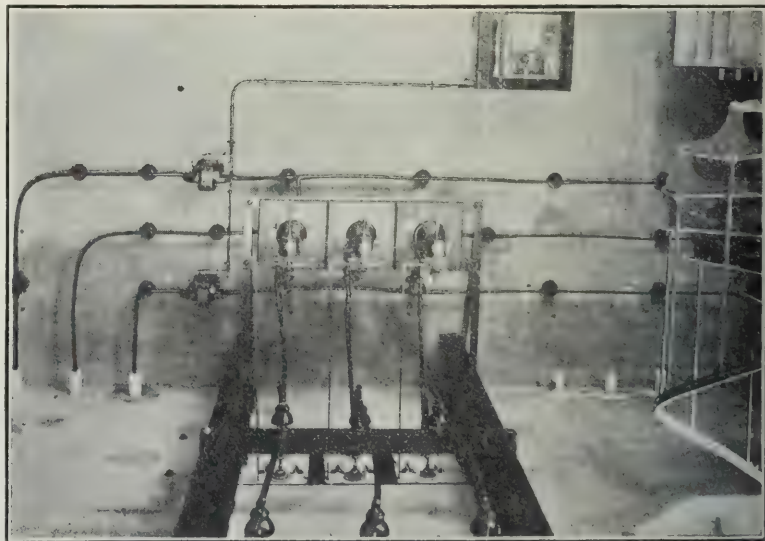


Fig. 20.

secondaries, oil-insulated, water-cooled, manufactured by the Packard Company. They are arranged in a line along the wall which separates the transformer room from the furnace room. Each transformer is controlled by a 2-pole, K-4, automatic remote-control, oil circuit-breaker in one leg of the circuit, the other

leg being connected to the bus-bar through a knife-switch. The circuit-breaker is mounted on a wooden framework alongside the transformer, and is controlled from the furnace room by iron connecting-rods. Knife-switches are mounted above the transformers, arranged to connect the transformers to any one of the three bus-bars, thereby keeping the load balanced. Copper bus-bars connect the transformers to the furnaces, the load on the furnace being regulated by a Thury regulator, manufactured in Geneva, Switzerland. A 500-kw. Packard water-cooled transformer is used for experimental purposes.

NORTON COMPANY.

The Norton Company has recently completed a new plant at Chippawa, Ontario, for the manufacture of crystolon. In this plant a modern transformer station has been installed whose function is to transform the high-voltage power generated by the Ontario Power Company at Niagara Falls to a lower voltage suitable for furnace work and induction-motor operation.

The transformer station proper is divided into two sections, namely, a room for the transformers and a room for the main-line switches, lightning-arresters, etc. The 3-phase transmission lines carried on the same pole line terminate in the switch-house and connect to knife-switches, cross-connected on the lower side so as to parallel the lines whenever both sets of switches are closed. From the knife-switches the current is conducted through choke-coils (Fig. 18) to a 3-pole, 300-ampere, form H₄, 13,000-volt Canadian General Electric Company oil circuit-breaker (Fig. 19) mounted on a concrete cell on a gallery on opposite side of switch-house. This gallery is reached from the main floor by a spiral stairway.

On the ground floor and to the right of the knife-switches are located four cells of aluminum lightning-arresters with horn-type spark-gaps, designed and manufactured by the Canadian General Electric Company.

The oil circuit-breaker mentioned above is unique in that the time limit relays for tripping the switches are made to carry the full high-voltage current of the line instead of being energized from current transformers (Fig. 20).

The relays are mounted on porcelain insulators directly below the gallery floor, with a tripping-rod passing up through the floor to a toggle-joint on top of the switch. On the floor beneath the gallery in concrete cells are located meter-potential transformers and fuses.

From the oil-switch the circuits pass through a wall to bus-bars in the main transformer room. These bus-bars are constructed of insulated wire supported on brackets and insulators fastened to the wall adjoining the furnace room (Fig. 21).

The main unit consists of a 750-kw. transformer with induction regulator in secondary circuit. The

transformer has a ratio of 12,000 volts to 145 volts, the regulator having a range of 75 volts up or down, which gives a voltage variation on the bus-bars, of 75 to 215 volts. Both transformers are of the oil-insulated, water-cooled type, the transformer being built by the Canadian General Electric Company and the regulator by the General Electric Company.

The transformer is protected by a 2-pole, 300-ampere automatic, K₄, Canadian General Electric, oil circuit-breaker mounted on an iron framework near the transformer. There are no walls or barriers between the switch-points, which are placed about two feet apart. Knife-switches connect the main unit to the bus-bars, and are arranged so that the transformer can be connected to either bus-bar. The 12,000-volt circuit is opened and closed through a water-switch, whose main elements consist of two

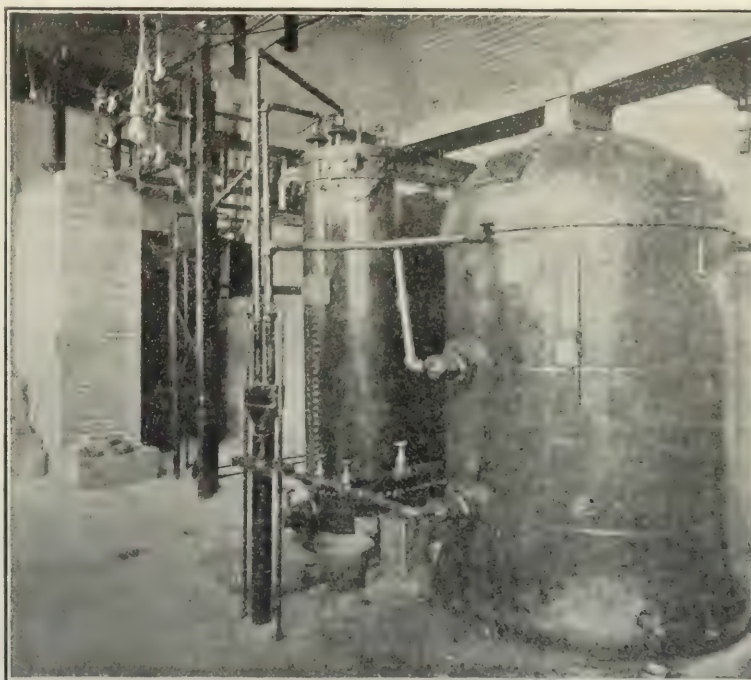


Fig. 21.

wooden barrels supported on porcelain petticoat insulators.

The motor load is provided for by three 40-kw., oil-insulated, self-cooled, Packard transformers, with 12,000-volt primaries and 440-volt secondaries connected in *delta*. A 3-pole, 300-ampere, automatic, K₄, oil circuit-breaker mounted on pipe framework controls these transformers. A small transformer bearing the name of the Packard Company, with a capacity of 15 kw., 110- to 120-volt secondary, supplies power for lighting the plant. This transformer is protected by out-door, Canadian General Electric expulsion fuses. On a small panel in the furnace room are located the indicating meters of the main unit. The switch handles that operate the oil circuit-breakers are mounted on a small marble panel in front of the iron framework carrying the oil pots. The transformer room and main building are of concrete

construction. The apparatus was installed by the Norton Company.

SMALL ELECTRIC FURNACE WITH HEATING ELEMENT OF DUCTILE TUNGSTEN OR DUCTILE MOLYBDENUM.¹

BY R. WINNI AND C. DANTSZEN

Received September 23, 1911.

There are many uses for a simple furnace which can be run higher than the melting-point of iron, and in which substances can be heated without taking up either carbon or oxygen.

There have been a few special furnaces, electrically heated, which are capable of fulfilling these conditions. Of these, we may mention the following:

1. The iridium-tube furnace. This is very fragile and extremely expensive.

2. A carbon-tube furnace with a porcelain tube inside. This makes an excellent tube-furnace, but calls for special transformers.

3. The platinum foil or wire-wound body of fire-clay or other refractory. This has been to the average man the most easily accessible and most generally used form of small furnace for fulfilling the conditions. But it has its limitations. Most serious of these are the fact that the platinum is easily contaminated, and that, except for small sizes, the winding is very expensive. Besides, this much of the work for which these furnaces are used necessitates running the platinum perilously close to its melting-point.

4. The Arsem vacuum furnace,² in which a graphite heater is used to generate the heat and in which the oxidation is prevented by the vacuum. This introduces carbon when very high temperatures are used.

We will show in the following how two simple types of furnaces have been made with a winding of ductile tungsten or molybdenum. It is now possible to produce these substances in the form of wire or ribbon, and their high melting-points and relatively low cost adapt them admirably to the purpose.

CRUCIBLE FURNACE.

This consists of a helix of ductile tungsten or molybdenum, supported by an alundum tube and protected from oxidation by a hydrogen atmosphere. The container, for the charge to be heated, is a small crucible which is placed inside of the alundum cylinder.

The diagram, Fig. 1, shows the furnace in vertical section. *W* is the heating wire, of ductile tungsten or molybdenum. It is wound on *G*, an alundum cylinder which is molded plain inside and with a helical groove on its outer surface. *A* is a Battersea crucible. *B* is an inverted Battersea of which the bottom has been cut off. *C* is the crucible bottom, used as a cover. The bottom of *A*, as well as the space between *A* and *B*, is filled with powdered silica. Hydrogen is constantly supplied to the furnace through the pipe *D*, and burns as it escapes from the top of *B*. This gives a protecting atmosphere for both the tungsten or molybdenum winding and the object to be heated.

¹ Presented at the General Meeting of the American Electrochemical Society, Toronto, September, 1911.

² These Transactions, 9, 153-172 (1906); *J. Am. Chem. Soc.*, 28, 921-935.

Current is supplied to the winding through two large copper connectors, *E, E*.

An object to be merely heated, as for annealing, may be inserted directly into the alundum cylinder.

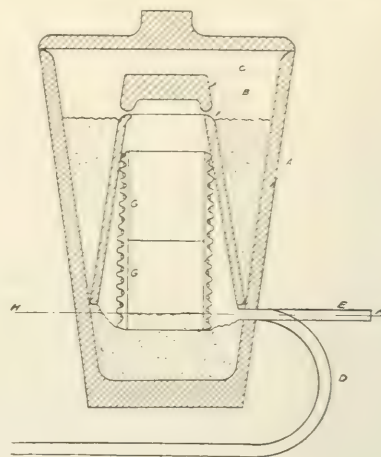


Fig. 1.

Material to be melted is placed in a small crucible, and this is let down into the alundum cylinder. An especially nice crucible to hold the charge is made of pure alumina.

A few dimensions and details of construction may be of interest.

In the apparatus shown in Fig. 1, the Battersea crucibles *A* and *B* are sizes *O* and *J* respectively. The alundum body *G* consists of two cylinders placed end to end. Each is 7.6 cm. high and 5.1 cm. inside diameter, while the distance from one convolution of the helix to the next is 0.95 cm. These alundum cylinders may be obtained from The Norton Company, of Worcester, Mass. The winding consists of 260 cm. square molybdenum wire, 1.27 mm. on a side. This wire is first wound on a mandrel 3.8 cm. in diameter, and wire and mandrel are then heated up to about 800° C. Upon then releasing the coil, it expands to the diameter of the alundum body, on which it can then be screwed. The copper connectors, *E, E*, are 0.8 cm. in diameter, and the ends of the coil are simply clamped in with set-screws. The copper connectors and the hydrogen inlet tube are held in place in the crucible wall by a mixture of powdered silica and water glass, which at the same time prevents loss of hydrogen.

This furnace can be safely run up to 1700° C. At this temperature it calls for 25 volts and 45 amperes.

We have melted pure iron and made many iron and other alloys in this furnace.

TUBE FURNACE.

This consists of a porcelain or alundum tube, wound with tungsten or molybdenum foil. Around the tube is a tight metal casing filled with powdered silica, and, to prevent oxidation of the winding, a hydrogen atmosphere is maintained in the casing.

Such a furnace is shown in the diagram, Fig. 2, in vertical length section. *A* is an alundum tube, 2.3 cm. inside diameter and 46 cm. long. The casing

D is made of thin sheet iron and is oxyacetylene welded. The winding is a molybdenum ribbon, 0.184 mm. thick, 2.54 mm. wide and 445 cm. long. *I, I* are heavy copper leads, fastened to the ends of

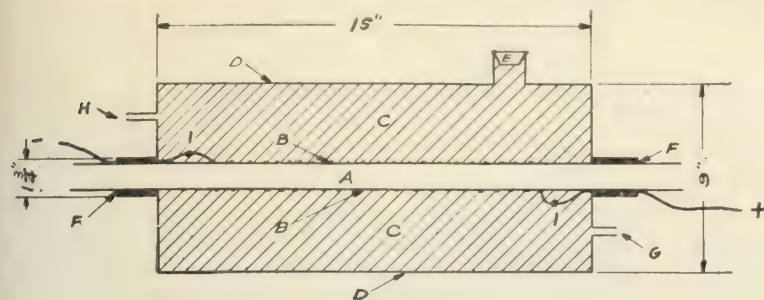


Fig. 2.

the coil by twisting the latter about them. *C* is the powdered silica packing; *F, F* is some asbestos wool, used to prevent the escape of hydrogen at the ends of the casing. *H* and *G* are the hydrogen inlet and outlet tubes respectively. *E* is a rubber stopper.

With this furnace a temperature of 1600° C. is readily attained. At this temperature it calls for 80 volts and 14.3 amperes.

The two furnaces above described are adapted to heating the charge in an atmosphere of hydrogen. In case it were desirable to heat in an oxidizing atmosphere, it would be necessary to replace the very porous alundum by porcelain, as otherwise the furnace winding would become oxidized.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.

DE LAVAL CENTRIFUGAL CLARIFIER AND FILTER.

The makers claim that in this machine they have solved the problem of the separation of solids from liquids—namely, the separation of a small amount of sediment, etc., from a solution—and that it has already stood the test of practice in the clarification and filtration of varnishes and allied products, oil pharmaceuticals, patent medicines, fruit syrups and extracts, in fact, of many liquids containing either a sediment deposit or the finest flock or both. But as this centrifugal machine will undoubtedly prove useful beyond its present sphere the following notes on its construction and operation should prove valuable.

An outside view of this machine is given in Fig. 1, which shows the steam-turbine style for direct steam connection. The largest size of this type has a height of 46 inches and requires a floor space of 18 inches by 24 inches, which indicates a big saving in floor space over other separating methods. In works where shafting is already installed the machine may be used with belt drive, while the smaller sizes of the machine are entirely practicable for running by hand.

Fig. 2 is a section of the clarifier and filter bowl. It contains the two compartments where the work is done, namely, the lower clarifying compartment and the upper filtering chamber.

The clarifying compartment consists of a cylinder filled with a series of conical-shaped, pressed-steel disks, one above the other, about $\frac{1}{32}$ inch apart and held rigidly in position by a central feeding device. The filtering chamber or upper section is also cylindrical in shape, but of less diameter.

The liquid first enters the bowl at the point *A* through the feeding device in the center and drops to the bottom of the clarifying compartments *B*, where much sediment is retained. It is then forced outward by the great centrifugal force through openings at the bottom to the periphery of the compartment *C*, where the bulk of heavier sediment is deposited. The liquid is next drawn to the center between the several disks. The purpose of these conical disks is to divide the liquid into thin layers, thus the friction on the disks above and below causes it to revolve rapidly and the heavier part, or balance of the sediment, is grad-

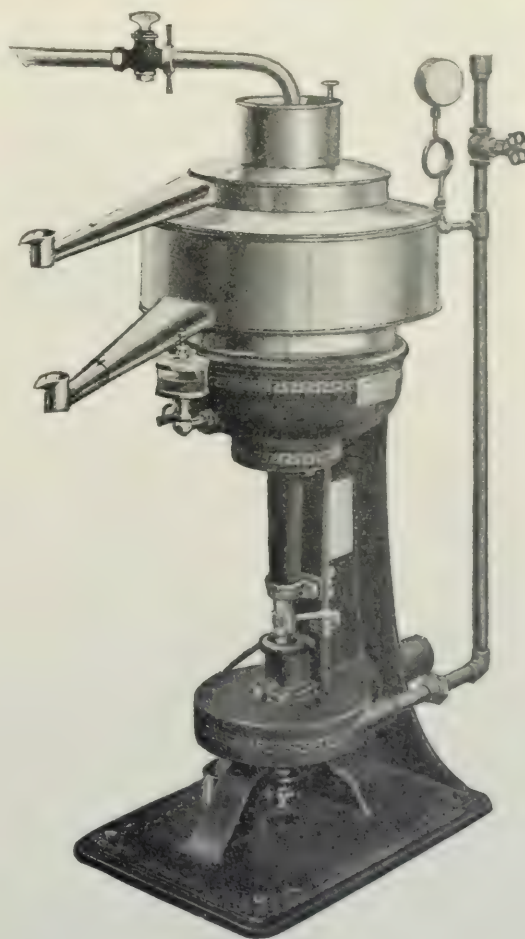


Fig. 1.

ually forced to the under side of the disk above, thence down and out to the pocket *C*, while the thoroughly clarified liquid passes to the center and is forced upward and out into the second or filtering chamber at *D*. When the liquid enters this compartment fully 99 per cent. of the sediment and foreign

matter has been removed, thus leaving a small though very important work for the filter to accomplish.

The filter chamber is filled with a series of horizontal corrugated plates and perforated retaining rings, between which are placed one or more thicknesses of

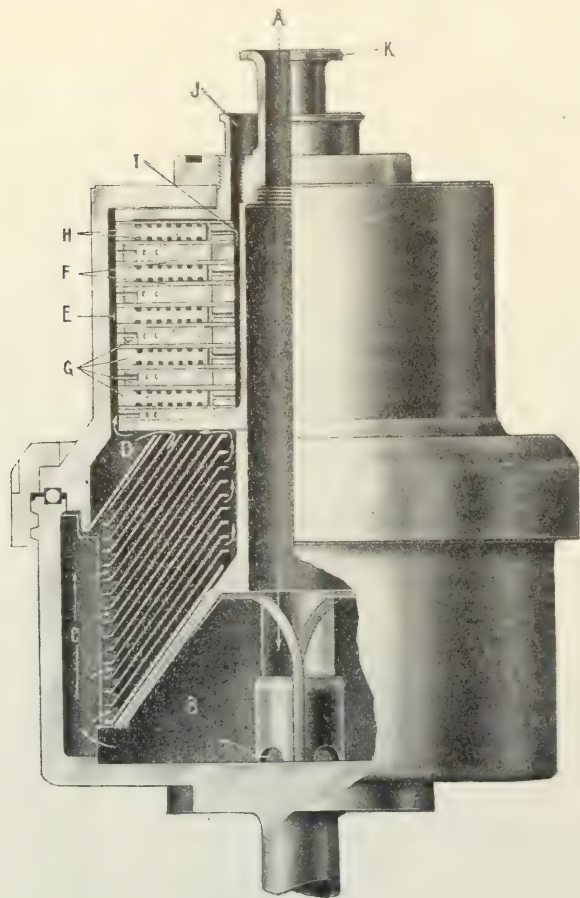


Fig. 2.

filter material, paper, felt, cloth or whatever may be best adapted to the work in hand. The liquid is forced from compartment D upward into the compartment E, which is a narrow space between the periphery of the filtering chamber and the filtering disks. This allows a channel for the liquid to pass up, from which it is delivered into the several compartments F, where it is forced through the filtering material G into compartment H. Here it is again forced to the center and upwards through channel I to the discharge point J and into the large cover from which it flows into the receptacle awaiting it.

The functions of the clarifying and filtering compartments supplement each other very thoroughly. The liquid is so thoroughly clarified by the disk system in the lower clarifying compartment that it leaves but a small amount of work for the filter to perform. Then, too, the filters being placed horizontally are substantially self-cleaning, for as the sediment or flock forms in any volume on the filters the centrifugal force throws it off and it is deposited at the outside or periphery of the compartments. Thus the filter material will do its work very much longer than

is possible otherwise and continue to deliver a product of the required fineness.

Where it is desirable to aerate the products to be handled, the separator can be made to automatically aerate the liquids as they pass through it and thus do away entirely with the necessity of air pumps or other equipment and labor necessary for aerating purposes with other filtering processes.

This machine is built by the De Laval Separator Company, 165 Broadway, New York City. The manufacturers state that with due care this clarifier and filter will last a lifetime. The average operator finds no trouble whatever in adjusting or cleaning any of the machine's parts and keeping it ever ready to perform its work. The chief advantages claimed for this machine are as follows:

The clarifier and filter will take any product to which it is adapted immediately after compounding and deliver continuously (except for occasional cleaning of the machine) a finished article ready for the market. It thus greatly reduces the capital necessarily tied up in settling tanks with other methods.

The manufacturer claims an average saving of 90 per cent. in filter paper and cloths and their subsequent washing and cleaning over that required by other processes, also a saving of liquid absorbed by the

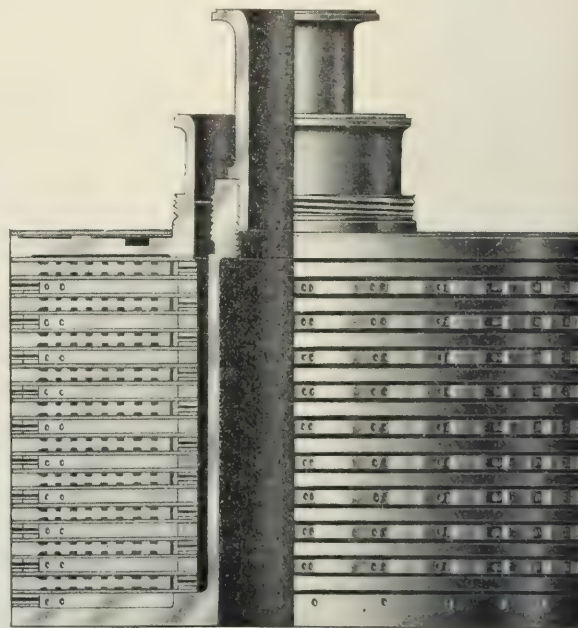


Fig. 3.

filter paper and that lost by evaporation or dripping with other methods, a saving of liquid, labor and the losses that sometimes occur from punctures in paper and a big saving in floor space.

AN AUTOMATIC PIPETTE.

By GEO. E. BOLTZ AND CHAS. J. SCHOLLENBERGER.

Received August 10, 1911.

Every analyst who makes a large number of determinations of the same character, each involving

the use of a constant volume of a solution, as of a caustic alkali, knows the amount of time and trouble required for measuring out the reagent used, and the generally unsatisfactory nature of such apparatus for this purpose, as that provided with glass stopcocks. Therefore, the following described automatic pipette was designed for the rapid measurement of the alkali hydroxide and sulphide solution used in the Kjeldahl method for nitrogen, but may be adapted to other uses as well.

The body (A) of the pipette is made of a section of wide glass tubing (the neck of a flask serves well), provided at the bottom with a rubber stopper perforated with two large holes; into each of these holes is fitted a short piece of glass tubing, one of which is

constructed and when properly made will deliver a volume of, say 50 cc., constant to within one-half cc.

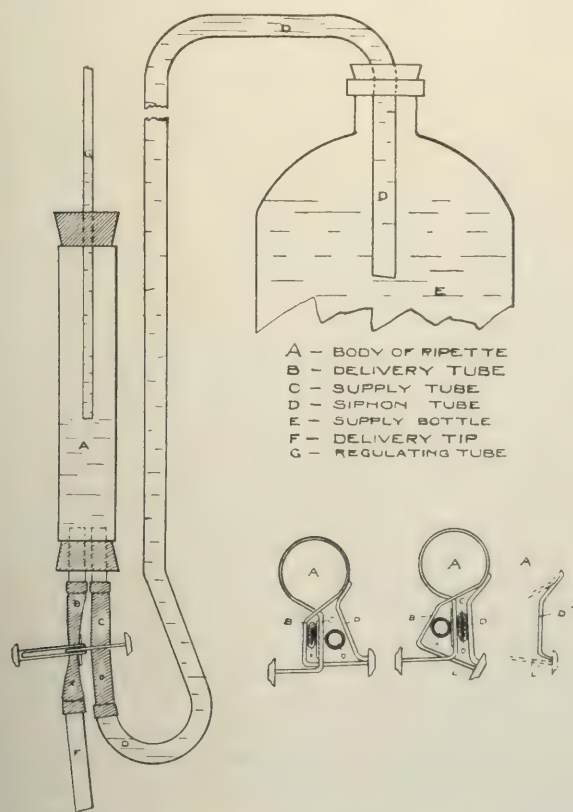
The writers desire to acknowledge their indebtedness to Mr. J. W. Ames, chief of the Chemistry Department of this Station, for his kindness in giving this device a practical trial.

OHIO AGRICULTURAL EXPERIMENT STATION,
WOOSTER, OHIO.

APPARATUS FOR RECEIVING AND MEASURING OIL OR NAPHTHA DISTILLED WITH STEAM.

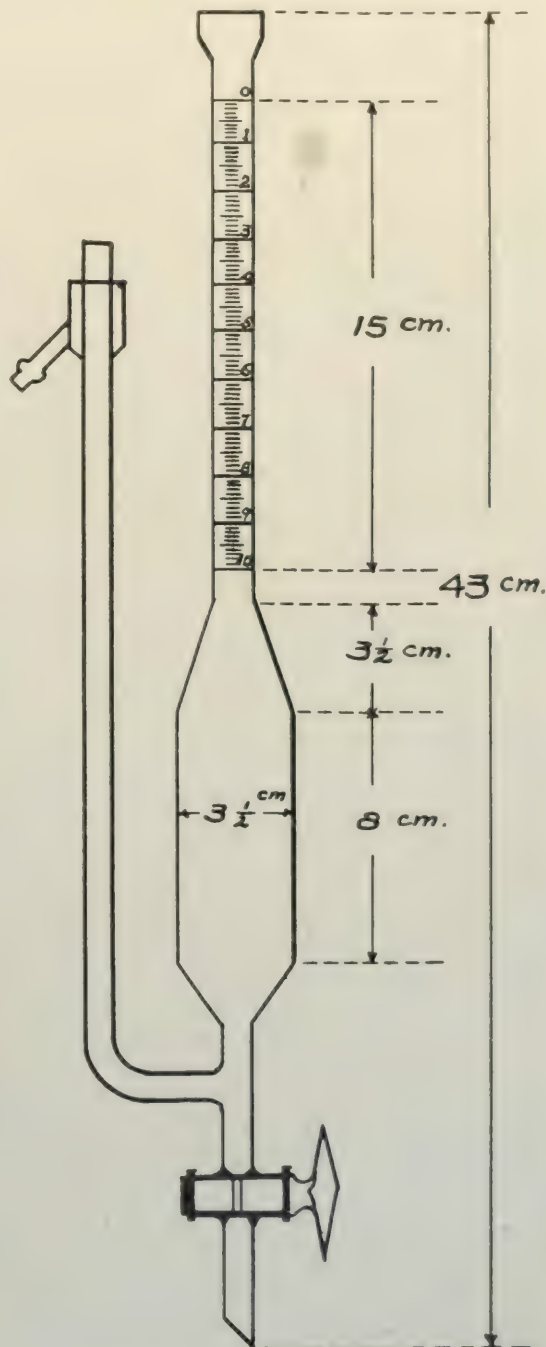
BY O. H. WURSTER

The naphtha content of a certain class of soaps and soap powders and the "oil" content of paraffine



connected to a siphon tube (D) for filling, bent as shown in the drawing, the other to a glass tip (F) for delivery, by suitable lengths (B) and (C) of rubber tubing. The top of the pipette is closed by a well fitting rubber stopper, carrying a single glass tube (G) of small diameter, which must be long enough to extend well above the level of the liquid in the supply bottle (E); by moving this tube in the stopper, the volume delivered by the pipette can be regulated.

A piece of strong steel wire, shaped as shown in drawing D", is soldered or preferably brazed securely to a heavy pinchcock of the common type; the completed article is shown in A and A'. This pinchcock is placed on the rubber tubes of the pipette so that tube X, for delivery, is normally compressed, and the pipette fills; on working the pinch-cock, O is closed, X for delivery opened, and the pipette is emptied. The apparatus is easily and cheaply con-



wax are frequently determined by distilling the naphtha or oil with steam. The distillation may cover a period of several hours. To facilitate the collection of condensed oil and water, and the measurement of the oil, the graduated receiver shown was designed. The naphtha collects in the calibrated

portion of the tube, and its volume can be read at any time. The water settles out and overflows automatically.

LABORATORY OF
M. WERK COMPANY,
CINCINNATI, Aug., 1911.

ADDRESSES.

SOME PROBLEMS IN CHEMICAL ENGINEERING PRACTICE.¹

By DR. F. W. FRERICHS.

Received Aug. 23, 1911.

The address, which I have prepared, comprises the development of three problems which actually have come under my observation. They were selected with a view of demonstrating the variety of questions, the solution of which may be expected from chemical engineers, the detail work which is necessary, and the care and training which are required for their successful solution.

The first problem solves the extraction of bismuth from ores. In this problem, the principal work is research, to develop the process which could be applied to the economical treatment of large quantities of ore. After the process was developed the translation into practice was comparatively simple and safe to predict.

The second problem treats the transplanting of a process from Europe to the United States and will prove that a process which is profitable in one location may be a failure under different conditions.

In the third problem the details of the process were known, and it was only required to construct complicated apparatus to carry out the process on a given scale.

In my opinion, problems similar to those represented could be used successfully for object studies in post-graduate work of chemical engineers, but it is necessary that the work be conducted by teachers, who themselves master the subjects, and who master them to such an extent that they readily would be willing to invest money of their own in the installment of plants, for which the research might be the foundation.

EXTRACTION OF BISMUTH FROM CARBONACEOUS ORES.

Bismuth is not of very rare occurrence and it can be produced greatly in excess of the consumption, which, in 1910, was about 200,000 pounds for the United States. The metal is used almost exclusively for medicinal preparations and its consumption does not materially vary with its price.

About ten years ago, being then a manufacturer of medicinal preparations, I looked for an independent supply of bismuth and turned my attention to Colorado, where I understood bismuth ores had been found. Personally going to Colorado, I examined the field but found everybody very reluctant to give information about bismuth ores. It was known that several lots had been mined in recent years, but there was

no market for it in the U. S., the smelters accepting it only for gold and silver values, charging a penalty for bismuth, since it deteriorated the lead, which was added in smelting the ores.

By the efforts of an assayer in Leadville, these lots of ores had been sold to a firm in England, where they were shipped by way of Galveston. It seemed to be a condition of the sale that the sellers were kept to secrecy and were not to sell subsequent lots to anybody else but the purchasers of the ore. If they should sell to any other party, contrary to the understanding, the buyers threatened not to buy any more ore from them.

This being the case, I could not secure any large lot of ore, but obtained a sample of several hundred pounds to make experiments.

The sample was a siliceous ore, had the appearance of yellow clay and was typical of ores carrying about one oz. of gold, 15 ozs. of silver, 5 per cent. bismuth, and 5 per cent. lead in the dry ore. A sample of the dry ore, finely powdered and treated with diluted muriatic acid, gave up all of its bismuth, except about 2 per cent, and these 2 per cent could not be extracted by concentrated muriatic acid. The mixture of ore with diluted muriatic acid was exceedingly slimy and did not readily filter nor did it settle.

Another sample of the ore was ignited in the open air for several hours, was finely powdered and would then give up all of its bismuth to diluted muriatic acid. The mixture was not slimy and filtered and settled fairly well. The amount of bismuth extracted in this manner from samples weighing from 100 to 1,000 grams corresponded well with the quantity of bismuth found by analysis in the original ore.

Analyses and extractions were repeated many times with ores from as many localities as I could get hold of, until I had full confidence in my analyses.

Being thus convinced that all the bismuth indicated by analyses of the ore could be extracted, and knowing that I could sell the gold and silver values in the tailings to one of the smelters, I believed myself to be ready to purchase a larger lot of ore, if opportunity should offer.

This opportunity presented itself sooner than I expected. A mine in which previously no bismuth ore had been found was nearing in its development an adjoining property in which bismuth ore had occurred and this mine had struck bismuth ore. The adjoining mine had produced several lots, running from 5 per cent. to 15 per cent. bismuth, 1 to 2 oz. of gold, and 5 to 10 oz. of silver. It seemed probable, but not certain, that a similar grade of ore could be

¹ Address read at the semi-annual meeting of the American Institute of Chemical Engineers, at Chicago, Ill., June 21, 1911.

taken from the new mine, and borings indicated large bodies of the material.

This mine offered to sell the entire output for a period of four years to my company. The mining company would not sell smaller lots from time to time, for fear that the English buyers would boycott them, in which case they would not have an outlet for their ore.

Desirous of obtaining possession of the ore, I negotiated a contract, by which my company agreed to take the entire output of the mine for a period of four years, which was estimated to be, and limited to the equivalent of 1600 tons of 5 per cent. ore, containing 160,000 pounds of bismuth. The ore was to be paid for its gold and silver values, as ascertained by fire assay and for bismuth as found by wet analysis.

The sampling of the ore was to be done by public sampler, buyer as well as seller supervising the work. The final sample reduced to a 100-mesh powder was to be divided into three parts, one to go to the buyer, one to the seller, and the third sample was to be held for the umpire, in case of disagreement of analyses made by buyer and seller.

The money value of the contract can be figured if I state that the ore delivered under this contract contained at an average 1 oz. gold and 100 ozs. silver, which would make the value of the ore \$180 per ton, figuring the 5 per cent. bismuth at \$1 per pound, which is equivalent to a total of \$288,000 for the entire contract.

This very large sum of money had to be paid out on values ascertained by analyses, and the confidence which I had in the correctness of my analyses and extraction tests may be measured by the fact that an error of $\frac{1}{10}$ of 1 per cent in the analyses or extraction test for bismuth would amount to \$3,200 for the entire contract.

In making the agreement I had to consider that settlements would be made on basis of analyses made by buyer and seller, and that an average of the two as a rule would be higher than the actual amount of bismuth contained in the ore.

I furthermore had to consider that there were few analytical chemists in Colorado who ever had made a bismuth analysis, and an error of 1 per cent or even more was of common occurrence. It was necessary that I be so sure of my methods of analyses and my results thereof that I could convince every analytical chemist of an error even if he was unwilling to admit it. In many instances I went to Colorado to straighten out differences, and always have succeeded in supporting my analyses. In one instance I spent about 10 days in Denver, during which time I compared, together with Dr. Albert H. Low, the basic chloride method with the electrolytical determination of bismuth, proving that under proper precautions both give the same results.

As far as I know, the results of this investigation have never been published. Therefore, I will give a short account of it, giving Dr. Albert H. Low full credit for the part he took in the investigation. Our

method of the determination of bismuth in ores is as follows:

Take 0.5 gram ore of No. 100 powder, treat in 250 cc. flask with 10 cc. strong nitric acid, and boil repeatedly until the acid is nearly gone. Add 10 cc. strong muriatic acid and heat gently until decomposition is as complete as possible. Dilute with 10 cc. hot water and filter, receiving filtrate in a 400 cc. beaker. Wash and filter residue thoroughly with warm diluted muriatic acid 1 to 3.

Nearly neutralize filtrate with aqua ammonia 10 per cent, dilute to about 300 cc. and precipitate bismuth, lead and other heavy metals with sulphuretted hydrogen. Filter and wash with hot water. Place filter and precipitate in a beaker and boil with 10 to 15 cc. diluted nitric acid 1 to 1 until the separated sulphur is clean and of white color and until the filter has been reduced to a pulp (which can be hastened by stirring with a glass rod). Dilute a little and filter into a 250 cc. flask, wash with diluted nitric acid 1 to 1 thoroughly and yet using as little as possible so as to keep filtrate of small bulk.

From this point on the analysis may be finished either by electrolysis or by the basic chloride method both of which are conducted as follows:

I. By Electrolysis.—Boil liquid in flask to small bulk, best by manipulating flask in a holder over a strong naked flame, and add 6 cc. of strong sulphuric acid. Continue boiling until sulphuric acid is fuming strongly. Cool and add 50 cc. water. Allow to cool, filter off the sulphate lead, and wash with a cold mixture of 6 cc. strong sulphuric acid and 75 cc. distilled water. Receive filtrate in beaker to be used for electrolysis and dilute to 200 cc. Electrolyze with current of 0.5 to 0.6 ampere and increase the current to 1 ampere towards the end of the operation. As cathode use a platinum cylinder 5 cm. long and 2.5 cm. in diameter. As anode use a platinum spiral made from 1 mm. wire.

For the electrolytic method the final solution should not contain more than 0.03 gram bismuth. If larger samples are taken bismuth is liable to drop off from the cathode and is difficult to collect. It is necessary to weigh in every instance the anode also, since small quantities of bismuth peroxide deposit there in protracted analyses, the amount of which must be added to the bismuth deposited on the cathode. The weights should be ascertained on a gold balance, weighing up to $\frac{1}{100}$ of one mg., and in careful work two analyses made from the same pulp would agree to within $\frac{1}{100}$ of 1 per cent for bismuth.

II. The Basic Chloride Method.—Receive filtrate in 400 cc. beaker and dilute with hot water to about 250 cc. Heat nearly to boiling and neutralize cautiously with water of ammonia 10 per cent., until an exceedingly faint opalescence is observed in the liquid. Dilute to about 350 cc. with hot water, add 1 cc. diluted muriatic acid 1 to 3 and 2 to 3 cc. of a saturated solution of muriate ammonium, cover the beaker and keep it nearly at boiling point until the basic chloride bismuth has settled clear or nearly so, filter and wash with hot water. The basic chloride bis-

muth obtained in this first precipitation may be contaminated with a little lead and for this reason it is dissolved on the filter in hot diluted nitric acid 1-1, and the precipitation of the basic chloride bismuth from the filtrate is effected in the same manner as described before. Finally, collect the basic chloride bismuth on a weighed filter, dry at 110° C. in the air bath and weigh.

Note 1.—If the ore contains arsenic or antimony, the precipitate made by treatment with sulphuretted hydrogen should be washed, first, with water and then two or three times with a warm solution of hydro-sulphurett ammonia and then again with hot water before proceeding.

Note 2.—In case the ore contains silver, this should be removed by adding a single drop of strong muriatic acid to the original diluted nitric acid solution before filtering. By shaking, the coagulation of the chloride silver should be facilitated, but care is to be taken not to dissolve it again by heating.

Note 3.—For quick working it is essential that no larger quantities of reagents and no larger vessels are used than indicated in the directions. If the directions are closely followed the determination of bismuth in ore can be carried out in four hours by either method.

Having received deliveries under the contract and having also secured several lots of ore and ore samples from other mines, laboratory tests of a great variety were carried out with these ores with a view of designing a process of extraction, which would fit as great a variety of ore as possible. The results of these laboratory tests could be tabulated as follows:

1. All bismuth ores to be considered were of siliceous character. The gangue had an average of

50	—	60	per cent. silica,
22	—	18	per cent. iron oxide,
19	—	15	per cent. alumina,
9	—	7	per cent barium sulphate,

— — —
100 100

and the ore contained 2 to 15 per cent. bismuth, 1 to 10 per cent. of lead by wet analyses, from 0 to 5 oz. gold, and from 1 to 150 oz. of silver by fire assay.

2. All ores had the appearance of yellow clay. If ground up in water they were very slimy, would not settle or filter, and the values could not be concentrated in the ore by the ordinary methods of concentration. The following experiments were carried out in a well equipped sampling and testing works with good machinery, and proved in all cases that too much bismuth remained in the tailings, and that only from $\frac{1}{2}$ to $\frac{2}{3}$ of the bismuth contained in the ore could be worked into a more concentrated form. In one instance in which a coarser ore had been used for the test from which the slime had been eliminated, the concentration of the bismuth was greater, but in no case a sufficiently concentrated ore could be obtained from which the bismuth could be separated by smelting in a satisfactory manner.

Exp. 1.—100 lbs. ore containing 11.80 per cent bismuth produced 13.2 lbs. concentrates containing

63.70 per cent—8.4 lbs. bismuth. 86.8 lbs. tailings containing 3.90 per cent—3.4 lbs. bismuth.

Exp. 2.—100 lbs. ore, containing 9.00 per cent bismuth produced 18.2 lbs. concentrates containing 31.20 per cent—5.68 lbs. bismuth. 81.8 lbs. tailings containing 4.05 per cent—3.32 lbs. bismuth.

Exp. 3.—100 lbs. ore containing 15.30 per cent bismuth produced 47.2 lb. concentrates, containing 30.40 per cent—14.35 lbs. bismuth. 52.8 lbs. tailings containing 1.80 per cent—0.95 lb. bismuth.

3. Raw ores would give up only 85 to 95 per cent of the bismuth contained therein to diluted hydrochloric acid, or to diluted solution of sulphuric acid and chloride of sodium. The bismuth so extracted was free of arsenic.

Example.—100 grams raw ore, No. 100 powder, containing 11.51 per cent bismuth by analysis extracted by 500 cc. of diluted muriatic acid 10 per cent, produced only 9.88 grams bismuth from the ore out of a possible 11.51 grams. The solution was only 19 per cent saturated and was liable to extract more than five times as much bismuth oxide. The extracted ore was filtered off and washed on the filter with 4 per cent muriatic acid until filtrate did not contain any more bismuth. The ore thus extracted, mixed with 500 cc. of 10 per cent muriatic acid and shaken in a machine for twenty hours, would not give up any more bismuth to the solution. 1.62 per cent bismuth remained in the ore and could not be dissolved by diluted muriatic acid, 10 per cent.

The same experiment was repeated with 100 grams of the same ore and a mixture of 500 cc. diluted sulphuric acid 13.43 per cent (which is equivalent to 10 per cent muriatic acid) and 80 grams chloride of sodium (the mixture measuring 531 cc.). All other conditions were the same as in the foregoing experiment. 9.667 grams of bismuth out of a possible 11.51 grams could be extracted, and this bismuth was free of arsenic while the ore contained this element in considerable quantity. The balance of 1.84 per cent bismuth could not be extracted by diluted acid solution, but its presence in the tailings could be proven by analysis.

4. Raw ores mixed with chloride sodium and subsequently roasted lose part of their bismuth by volatilization.

Experiment.—300 grams raw ore, containing 1.84 per cent bismuth mixed with 30 grams chloride of sodium and roasted in a muffle furnace for six hours to dark red heat, contained after roasting only 0.3 per cent bismuth by electrolysis.

5. Raw ores, reduced to a No. 30 mesh powder and subjected to an oxidizing roasting for several hours, settle and filter fairly well, and in this form the ore is fit for extraction.

6. Roasted ores, especially if they are moistened with small quantities of sulphuric acid before roasting and reduced to a No. 30 powder, will give up all of their bismuth to an excess of cold diluted muriatic acid or to an equivalent solution of sulphuric acid and chloride of sodium, but the bismuth so extracted contains arsenic.

Experiment 1.—Three samples of 100 grams each of roasted ore, No. 30 powder, containing 11.51 per cent bismuth, were extracted each with 250 cc. solution sulphuric acid, 13.43 per cent, and 40 grams chloride of sodium. The samples were shaken in a machine for one, two and twelve hours, respectively, at 15° C. In each case 100 cc. of the filtrate were precipitated with 1500 cc. of water and the basic chloride of bismuth was filtered off, dried and reduced to metal by melting with cyanide potassium and from the weight of the bismuth, the amount contained in the entire solution was calculated.

Sample No. 1, shaken 1 hour, produced 11.25 grams bismuth.

Sample No. 2, shaken 2 hours, produced 11.11 grams bismuth.

Sample No. 3, shaken 12 hours, produced 11.44 grams bismuth which proved practically complete extraction of bismuth from the roasted ore. The acid in these cases was very much in excess of the bismuth oxide contained in the ore for which reason the solutions were very acid, requiring much water for precipitation; besides there was a great waste of acid. With less acid, extraction would not be complete.

Experiment 2.—2,000 grams of dry, raw bismuth ore, No. 100 powder, containing 11.51 per cent bismuth by analysis, mixed with a solution containing 4,000 cc. diluted sulphuric acid, 13.43 per cent, and 640 grams chloride of sodium, were shaken in the machine for fourteen hours, and gave, upon filtration, which was not followed by washing, 3186 cc. filtrate, measuring equal to 7.6 per cent muriatic acid by titration. This solution, upon precipitation with much water, separated sufficient basic chloride bismuth to make 139.0 grams bismuth metal by melting with potassium cyanide.

The material, which remained on the filter, was washed with 1,000 cc. diluted muriatic acid 7 $\frac{1}{2}$ per cent, and drained until 1,000 cc. had filtered off. From this filtrate the basic chloride bismuth was precipitated, and made 15.6 grams bismuth by melting with potassium cyanide.

The washing of the material on the filter was followed up with three subsequent washings, the first time with 2,000 cc. of 5 per cent muriatic acid, the second time with 2,000 cc. of 3 per cent, and the third time with 2,000 cc. of 1 per cent muriatic acid. In each washing, 1750 cc. filtrate were collected from which 14.9 grams, 8.9 grams, and 4.4 grams, respectively, of bismuth metal were obtained by melting the basic chloride bismuth with potassium cyanide.

The last washing was done with 200 cc. water and the resulting filtrate yielded 0.7 gram bismuth.

The exhausted ore weighed 1675 grams after drying. It was moistened with 65 cc. strong sulphuric acid and roasted in a muffle furnace for four hours at a dark red heat.

After roasting it was extracted again with a solution made up from 3,000 cc. sulphuric acid, 13.43 per cent, and 480 grams chloride of sodium. The extraction was accomplished by shaking the mixture 14 hours in a machine and after precipitating the

solution and melting the basic chloride bismuth with potassium cyanide, 29.5 grams bismuth were recovered.

The tailings from the second extraction proved still to contain 0.28 per cent. bismuth by electrolysis.

The results of the successive extractions are entered in Table I.

TABLE I.—EXTRACTION OF BISMUTH FROM ORE BY SUCCESSIVE TREATMENT WITH ACID SOLUTIONS.

2,000 grams of dry, raw bismuth ore, No. 100 powder, containing 11.51 per cent bismuth, extracted with 4,248 cc. of a solution made from 4,000 cc. diluted sulphuric acid 13.43 per cent, and 600 grams sodium chloride

	Extracting solution. cc.	Acidity equal per cent HCl.	Filtrate. cc.	Bismuth extracted. Grams.
1st extraction.....	4248	10.0	3186	139.0
2nd ".....	1000	7.5	1000	15.6
3rd ".....	2000	5.0	1750	14.9
4th ".....	2000	3.0	1750	8.9
5th ".....	2000	1.0	1750	4.4
6th ".....	200	0.0	?	0.7

Total bismuth free of arsenic..... 183.5

1,675 grams tailings roasted with 65 cc. concentrated sulphuric acid and extracted made bismuth..... 29.5

Tailings from second extraction had 0.28 per cent bismuth... 4.6

Lost in roasting and otherwise..... 12.6

Total, grams..... 230.2

7. Roasted ores cannot readily be extracted by diluted sulphuric acid, 13.43 per cent, without the addition of chloride sodium.

8. Roasted ores surrender their bismuth to 10 per cent hydrochloric acid or to an equivalent solution of sulphuric acid and chloride sodium completely only upon boiling, making fairly neutral solutions.

Experiment.—Roasted ore, containing 4.99 per cent of bismuth after extraction with diluted sulphuric acid and chloride sodium, showed only 0.03 per cent bismuth in the tailings.

By these observations, the conclusion has been reached that the extraction of the bismuth from the ore by diluted muriatic acid would be most complete and at the same time economical. The latter was particularly so since a diluted solution of sulphuric acid and chloride sodium in the proportion of the molecular weights could be substituted for hydrochloric acid. Cheap sulphuric acid manufactured as a by-product from the roasting process of zinc ores was at my disposal.

For this reason it was decided to work out systematically a process of extracting bismuth from the ore by diluted hydrochloric acid and also by diluted solution of sulphuric acid and chloride sodium of the same acidity.

The general idea of the work was to obtain a solution of bismuth chloride, to precipitate bismuth in the form of basic chloride bismuth by addition of much water, and to recover the metal values remaining in the solution by sodium sulphide in form of a black precipitate of metallic sulphides. From the basic chloride of bismuth, the metal was to be obtained by melting with charcoal, soda, and chloride of potassium; the metal sulphides after roasting were to be worked up by methods suitable to extract the various metals from them.

The chemical reactions and properties of materials involved in these operations were first studied on pure chemicals.

1. The solubility of basic chloride bismuth in diluted muriatic acid of various strengths.

These determinations were made by shaking in a shaking machine for eight to twelve hours at a temperature of 15° C. a flask containing 500 cc. diluted acid solutions of various strengths with an excess of basic chloride bismuth of high purity, free of bismuth hydroxide. In the resulting solution, after filtering, the acid as well as the basic chloride bismuth were quantitatively determined by the following method:

10 cc. of the solution were titrated with normal solution caustic alkali (phenolphthalein serving as indicator). By special experiment it had been proven that all of the bismuth had been precipitated from the solution as basic chloride bismuth a little before the moment, when the phenolphthalein turned pink, and the number of cc. of the normal solution caustic potassa indicated the amount of acid, which held the basic chloride bismuth in solution.

In a second sample of 10 cc. of the same solution, the bismuth was determined by precipitation and weighed as bismuth oxide. The values found for the solubility of basic chloride bismuth in diluted muriatic acid of various strengths are entered in Table II.

TABLE II.—SOLUBILITY OF BASIC CHLORIDE BISMUTH IN MURIATIC ACID OF VARIOUS STRENGTHS.

Bi, 208; Cl, 35.5.

Basic chloride bis- muth free of oxide.	Diluted acid used.		10 cc. filtered solution			
	Grams.	cc.	con- tain- ing HCl. Per cent.	Time of shak- ing. Hrs.	contain:	
					Bi ₂ O ₃ .	BiOCl.
					Grams.	Grams.
						are equal normal solution KOH. cc.
10	500	1	36	0.0015	0.0017	2.7
20	500	2	36	0.0225	0.0252	5.5
30	500	3	36	0.112	0.125	8.3
40	500	4	36	0.251	0.281	11.0
50	500	5	36	0.413	0.462	13.75
60	500	6	12	0.550	0.615	16.4
70	500	7	12	0.767	0.858	19.1
80	500	8	12	0.963	1.077	22.0
90	500	9	12	1.157	1.294	24.6
100	500	10	12	1.398	1.562	27.4

2. The solubility of basic chloride in a diluted solution of sulphuric acid and chloride sodium of an acidity equivalent to 10 per cent hydrochloric acid is somewhat less than the solubility in pure diluted muriatic acid. Exact determinations were made in the same manner as described in the determination of solubilities in muriatic acid.

As an average of two determinations, it was found that 71.57 grams of basic chloride bismuth could be dissolved in a solution made from 500 cc. sulphuric acid, 13.43 per cent, and 80 grams chloride of sodium, while 78.10 grams basic chloride bismuth could be dissolved in 500 cc. of diluted muriatic acid, 10 per cent.

3. The solubility of basic chloride bismuth in very diluted muriatic acid was ascertained in the same manner as the solubility in diluted hydrochloric acid from 1 to 10 per cent, as described above, and the values found were entered in Table III:

TABLE III.—SOLUBILITY OF BASIC CHLORIDE OF BISMUTH IN VERY DILUTE MURIATIC ACID.

Bi, 208; Cl, 35.5.

BiOCl used.	Diluted HCl				10 cc. filtered solution			
	normal HCl. cc.	mixture contains water. cc.	HCl. Per cent.	Time of shaking. Hrs.	contain		are equal to normal sol. KOH	
					Bi ₂ O ₃ .	BiOCl.	found.	should be.
					Gram.	Gram.	cc.	cc.
4	40	460	0.292	8	none	none		
6	60	440	0.438	8	none	none		
8	80	420	0.584	8	none	none		
10	100	400	0.730	8	none	none	1.9	2.0
20	200	300	1.460	8	0.0067	0.0075	3.9	4.0
30	300	200	2.190	8	0.0300	0.0335	5.5	6.0
40	400	100	2.920	8	0.0863	0.0965	7.7	8.0
50	500	...	3.650	8	0.1590	0.1778	9.7	10.0

This table is slightly incorrect, since the basic chloride bismuth used for this determination contained a trace of bismuth oxide. For this reason the figures in the second last column are slightly smaller than they are in the last column. For practical purposes, however, the values of the table were considered sufficiently correct.

4. Precipitation of basic chloride bismuth from its solution in diluted hydrochloric acid, and in solutions of diluted sulphuric acid and chloride sodium by diluted alkali solutions.

It was ascertained that a normal solution of caustic potassa gradually added to a solution basic of chloride bismuth in diluted hydrochloric acid, or in a diluted solution of sulphuric acid and chloride sodium, will precipitate basic chloride bismuth, and if phenolphthalein is used as an indicator, the solution will turn pink at the moment when all of the solvent acid is neutralized.

A little prior to this point all of the basic chloride bismuth was precipitated from the solution.

5. The properties of solutions obtained by extracting bismuth ores with diluted solutions of sulphuric acid and chloride of sodium must necessarily vary since, in addition to bismuth, more or less iron is extracted from the ore. A mixture of 1100 parts by weight of sulphuric acid, 13.43 per cent (12.5° Beaumé), and 160 parts chloride of sodium, having a specific gravity of 23° Bé., was found most suitable for extracting the ore. This acid mixture filtered through rich bismuth ore, containing 7 to 12 per cent of the metal, increases its specific gravity to 40° Bé., however, in the same proportion as the ore becomes exhausted, the specific gravity of the filtrate decreases, and the percentage of bismuth contained therein is growing less. Table IV gives the approximate relation between specific gravity of the filtrate and of the bismuth contained in same.

TABLE IV.—RELATION OF SPECIFIC GRAVITY OF BISMUTH CHLORIDE SOLUTIONS CONTAINING SULPHATES AND BISMUTH CONTAINED IN SAME.

°Bé.	100 cc. contain		°Bé.	100 cc. contain		°Bé.	100 cc. contain	
	Bi gr.			Bi gr.			Bi gr.	
25	0.2		31	5.3		37	8.5	
26	1.1		32	6.0		38	8.9	
27	2.0		33	6.6		39	9.3	
28	2.9		34	7.1		40	9.7	
29	3.7		35	7.6		41	10.1	
30	4.5		36	8.1		42	10.5	

It is not desirable to work with solutions which are

stronger than 40° Bé., since they tend to crystallize at temperatures below 15° C. and are liable to prevent the filtering of the solutions through the ore.

In order to ascertain the degree of dilution with water necessary to precipitate the basic chloride bismuth from this solution, the following determinations were carried out:

100 cc. bismuth solution, 40° Bé., 300 cc. water precipitate, 9.0 grams basic chloride bismuth.

100 cc. bismuth solution, 40° Bé., 400 cc. water precipitate, 10.1 grams basic chloride bismuth.

100 cc. bismuth solution, 40° Bé., 500 cc. water precipitate, 10.0 grams basic chloride bismuth.

And in using a different solution:

100 cc. bismuth solution, 500 cc. water precipitate, 13.1 grams basic chloride bismuth.

100 cc. bismuth solution, 1000 cc. water precipitate, 12.9 grams basic chloride bismuth.

100 cc. bismuth solution, 1500 cc. water precipitate, 12.8 grams basic chloride bismuth.

These experiments indicate that dilution of a concentrated solution with five times its volume of water will precipitate practically all of the bismuth which is in solution.

6. Recovering the metal values from the solutions resulting from the precipitation of basic chloride bismuth.

The valuable metals which could remain in the solution could all be precipitated by sulphuretted hydrogen, and precipitation with sulphide of sodium from the acid solution proved to be the cheapest way to accomplish this end.

A solution obtained by boiling 690 pounds of caustic soda, 74 per cent, 460 pounds of sulphur flour and sufficient water to make 40 cu. ft. was found suitable for the purpose. The sulphides of the heavy metals settled quickly and the resulting solutions were run to waste. The metal sulphides were collected, dried, and roasted for the purpose of eliminating sulphur and the roasted product in one instance was found to contain 54.9 per cent bismuth, 4.3 oz. silver, and 0.40 oz. of gold. This material was worked up by extraction with diluted acid in the same manner as the ore itself.

7. The reduction of basic chloride bismuth to metal could be accomplished by melting it with a mixture of chloride potassium, carbonate sodium and powdered charcoal, and the resulting metal could be purified by melting with a very small quantity of caustic soda and nitrate of potassium.

After these preliminaries, the arrangement of a larger plant for the extraction of bismuth ore suggested itself, and the operations which were to be executed on a larger scale were as follows:

A. To prepare the ore for extraction.

B. To extract the ore by acid solutions.

C. To recover the values from the solutions.

D. To prepare the extracted ore for shipment to smelters, where it was to be treated for its values of gold, silver, and lead.

A. *Preparation of the Ore for Extraction.*—The raw ore as it came from the mines was in a lumpy condi-

tion and contained from 10 to 15 per cent moisture. Treated with water, it would form a slimy mixture which would not filter or settle. It could not even be filtered in filter presses or on suction filters. It would not give off all of its bismuth to diluted muriatic acid, unless it had been roasted in the open air. The ore was dry enough to run through an ore crusher in which it could be reduced to $\frac{1}{2}$ inch size. Subsequently it was dried on a drying floor and ground in a suitable mill to No. 30 powder. Finally, the ore was roasted for four hours in a reverberating furnace to dark red heat, air being admitted freely to effect an oxidizing roasting process.

The roasted ore consisted of a dark red powder, all of which passed through a No. 30 sieve, and about 25 per cent of it would run through a 100-mesh bolting cloth. The mixture of the roasted ore powder and diluted muriatic acid, after boiling, would settle and filter fairly well, and in this condition the ore seemed to be well prepared for extraction with diluted hydrochloric acid or a diluted solution of sulphuric acid and chloride of sodium.

The plant which was used for this operation is outlined in Fig. 1.

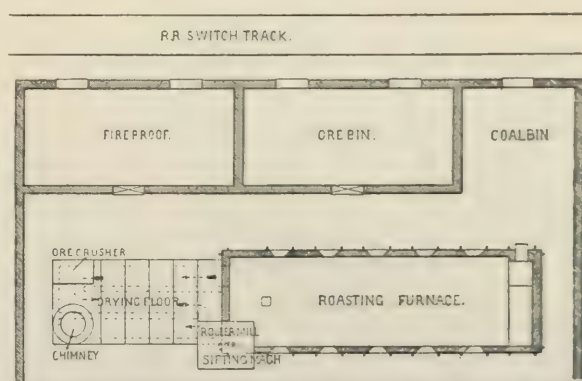


Fig. 1.—Plant for grinding and roasting bismuth ore.

A line of fire-proof ore bins was adjoining a switch track from which the ore was unloaded from the railroad cars. These ore bins having a granitoid floor afforded good opportunity for sampling the ore. From these bins the ore was taken to the crusher, from which it was discharged about $\frac{1}{2}$ inch size directly to a drying floor, measuring 20' x 10' 6". The dry ore was run through roller mills and sifting machine, and as No. 30 powder was charged into the roasting furnace which was 40' long and 12' 9" wide, outside measurements. The capacity of this plant was about 8 tons of dry ore per day of 24 hours, which was more than could be worked by the lixiviation plant. But it did not seem economical to install a smaller furnace and intermittent operation was decided on.

B. Extraction of Bismuth from Roasted Ore by Acid Solutions.—The problem was to extract from the ore as it came from the roaster, and which was in the shape of a No. 30 powder, about 25 per cent. of which would pass a 100-mesh sieve, all of the bismuth with as little acid solution as possible, obtaining

the most concentrated solutions, and to recover all of the metals from these solutions.

The preliminary experiments had proven that all of the bismuth could only be extracted by boiling the roasted ore with acid solutions, and in the course of operations it was found expedient to separate immediately after boiling the fine parts from the coarser material of the ore by settling and to work each in separate operations.

An apparatus of the general arrangement outlined in Fig. 2 was thought to be suitable for this work.

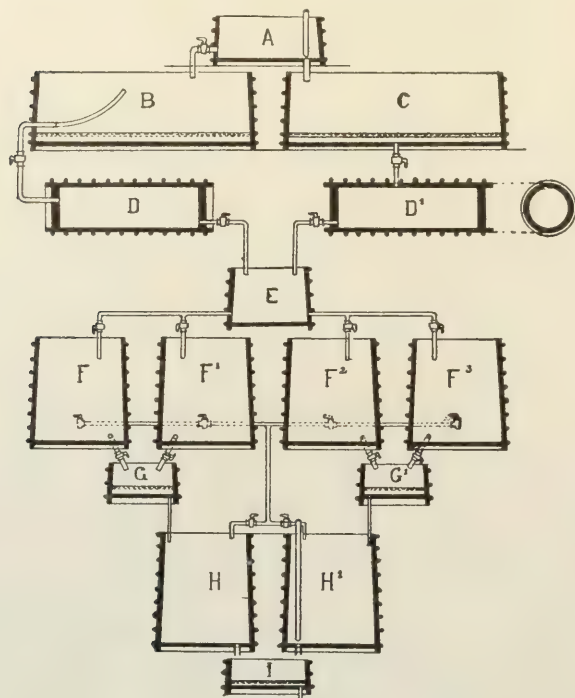


Fig. 2.—Plant for extracting bismuth ore.

The size of the various tanks were arrived at by the following considerations:

A round boiling tank, 8' diameter and 3' high, seemed to be the largest size in which ore could be boiled with acid solutions, allowing at the same time agitation of the ore by hand. A tank of that size would take the following charge:

3,000 pounds roasted ore, having about 5 per cent. bismuth.

1,200 pounds sulphuric acid, 60° Bé.

1,110 pounds sodium chloride.

q. s. water to make 100 cu. ft. liquid.

This charge was boiled by live steam under constant stirring.

The contents of the boiling tank were separated right after boiling by running most of the solution, in which the slimes were suspended, into a vacuum filter of suitable size, whereupon the coarse settleings in the boiling tank were shoveled into another vacuum filter. 85 cu. ft. of bismuth solution could be filtered off at a vacuum of 15 inches mercury in twelve hours.

In working this particular lot of ore, a bismuth solution of 34° Bé. could be obtained, 10 cc. of which admitted of an addition of 3 cc. normal alkali solution

before a turbidity, caused by precipitation, of basic chloride bismuth would appear.

The 85 cu. ft. bismuth solution, diluted with twice its volume of water, precipitated sufficient basic chloride bismuth to make 141 pounds of bismuth by melting, which indicated that 8½ pounds bismuth were contained in the solution which could not be separated from the ore without washing.

The slimes remaining in the filter tank after draining consisted of about 8 cu. ft. of very sticky material, containing 28 per cent. moisture.

The coarser ore in the other filter tank measured about 30 cu. ft., contained 14 per cent moisture, and had in a moist state a weight of 88 pounds to the cu. ft.

To accommodate the coarse tailings from 50 tons ore in one ore filter, a space of 1,000 cu. ft. was necessary, and a round filter tank, "C," of 16 ft. diameter and 6 ft. high was erected for the work.

A settling filter, "B," of the same size as ore filter "C" was provided for the slimes, and this was arranged in such a manner that the larger part of the clear liquid could be drawn off from the top after settling, while only a small proportion needed to filter through the slimes.

Vacuum vats "D" and "D'", 3 ft. diameter and 12 ft. long, were connected with the filters, and a vacuum of 10 to 15 inches mercury was maintained in same.

C. Recovering the Values from the Solutions.—It was found necessary to have four precipitating tanks, F, F', F², and F³, each 7' diam. and 8' high, for the purpose of precipitating basic chloride bismuth, and 2 precipitating tanks, H and H¹, of the same size for sulphides, in order to keep up with the work in the boiling tank.

Two filter vats, G and G', 5' diameter and 2' high, served for draining the basic chloride bismuth, and one filter vat of the same size and marked "I" in the drawing, for draining the sulphides.

The capacity of the plant proved to be six tons of 5 per cent bismuth ore per day. This work could be carried on for about eight days, until the ore filter was full of coarse tailings and it required from 3 to 6 days to wash the material on the filter and get ready for a new lot.

The average capacity was about 100 tons per month, if 5 per cent ore was worked. Ores containing less bismuth could be worked quicker, while richer ores required a longer time for boiling and lixivation.

Metal sulphides were collected from time to time on filter I and, after drying and roasting, they were extracted in the same manner as the ore. A lot of 848 lbs. of roasted sulphides containing 42 per cent. lead and bismuth by fire assay, besides 15.2 ounces of silver and 1.6 ounces of gold to the ton of material.

The basic chloride bismuth was dried in iron kettles and the metal was obtained from it by melting in iron kettles with soda ash, potassium chloride, and charcoal.

The iron kettles used for this purpose were 22 inches

in diameter and 20 inches deep and had a fairly flat bottom, slightly dished to the center.

One man and one helper could dry and melt in 3 kettles, operating them at the same time. A suitable charge for melting in one kettle was 40 pounds basic chloride bismuth, 6 pounds potassium chloride, 12 pounds soda ash, 58 per cent, and 8 pounds of powdered charcoal.

TABLE V.—COST OF EXTRACTING BISMUTH FROM ORES BY DILUTED SULPHURIC ACID AND CHLORIDE OF SODIUM

Cost of treatment per ton of ore. St. Louis prices.

Average quantities used in working ore lots containing varying amounts of Bi.	113 tons dry ore containing 2 per cent. Bi.			44.5 tons dry ore containing 4.75 per cent. Bi.			235.5 tons dry ore containing 6.26 per cent. Bi.		
	Lbs.	Cents.	Dollars.	Lbs.	Cents.	Dollars.	Lbs.	Cents.	Dollars.
Sulphuric acid, 60° Bé.....	1115	0.4	4.46	1101	0.4	4.40	1107	0.4	4.43
Chloride sodium, 90 per cent., inferior quality.....	1115	0.2	2.23	1101	0.2	2.20	1107	0.2	2.22
Caustic soda, 74 per cent.....	44	2.4	1.06	82	2.4	1.97	89	2.4	2.14
Sulphur flour.....	30	1.2	0.36	55	1.2	0.66	61	1.2	0.73
Time.....			13.47			15.67			16.40
Coal for roasting, \$1.50 per ton.....	1910		1.43	3240		2.43	3660		2.75
Sundries, repairs, steam.....			5.00			5.00			5.00
Cost of treatment									
Weight of chemicals } per ton of dry ore.....	2304		\$28.01	2339		\$32.33	2364		\$33.67
Weight of coal }.....	1910			3240			3660		

In one instance, one man and one helper made in 8 working days, from 1,672 pounds basic chloride bismuth, 252 pounds potassium chloride, 504 pounds soda ash, 58 per cent, and 336 lbs. powdered charcoal, a total of 1,241 pounds of bismuth metal, which by melting with $2\frac{3}{4}$ pounds of caustic soda, 74 per cent, and $5\frac{1}{2}$ pounds of nitrate potassium had been freed from arsenic.

In another instance, one man and one helper reduced, in 8 working days, 1,229 pounds of bismuth metal from 1,612 pounds basic chloride bismuth, 240 pounds potassium chloride, 480 pounds soda ash, 58 per cent, and 320 pounds powdered charcoal.

D. The extracted ore was dried on a heated floor. The coarse material and the slimes were kept separate, and after sampling the material was ready for shipment to the smelters.

By the process and with the plant described, about 1,000 tons of ore were treated, and somewhat more than 60,000 pounds of bismuth were extracted from the ore.

Table V gives a comparison of the cost of working ores, containing 2 per cent, 4.75 per cent and 6.26 per cent bismuth, respectively.

Table VI gives a comparison of the cost of treating 6.26 per cent. ore in Leadville and in St. Louis.

TABLE VI.

If the ore is treated in Leadville, where the tailings can be sold to the Leadville smelter, thus saving freight, the cost of extracting bismuth from 6.25 per cent ore changes as follows:

Basis: Lot weighing 530,870 lbs. gross (wet).

471,138 lbs. dry.

Savings over St. Louis prices:

Freight on ore to St. Louis.....	\$2,256.20
Switching.....	53.08
Unloading.....	53.08
Purchasing expenses, $\frac{2}{3}$	200.00
Freight on tailings to smelter.....	464.15

\$3,026.51

Larger expenditures than in St. Louis:

Freight on 278 tons chemicals, at \$15.00.....	\$4,170.00
Excess cost of 431 tons coal, at \$1.50.....	646.50

\$4,816.50

These figures are in favor of St. Louis.

From Table V it is seen that the cost of extracting low-grade ore is less per ton of ore than the treatment of ore containing more bismuth. But the cost of extracting 100 pounds bismuth from high-grade ore is much less than from inferior material.

Table VI shows that the cost of extracting bismuth ores is higher in Leadville than in St. Louis, principally on account of the freight charges on coal and chemicals.

TABLE VII.—COST OF BISMUTH EXTRACTED FROM LEADVILLE ORES

Weight of ore: 530,870 lbs. gross (wet).

471,138 lbs. dry.

Assay: Silver, 83.53 oz. per ton. Bismuth 6.26 per cent. in the dry ore.
Gold, 1.09 oz.

Conditions of Purchase: Silver paid for at 95 per cent. of New York market quotations; Gold paid for at \$19.40 per ounce; Bismuth $1\frac{1}{2}$ per cent. deducted from values found by wet analysis to compensate for treating charges, the rest to be paid for at the rate of 77.5 cents per pound bismuth in the ore. Freight to St. Louis paid by seller.

Values contained in the ore by assay.	Values paid for		
Silver, 19,679.00 oz.....	18,695.00 oz.	\$ 0.55	\$10,282.25
Gold, 256.35 oz.....	256.36 oz.	19.40	4,973.19
Bismuth, 29,503 lbs.....	22,436.00 lbs.	0.77 $\frac{1}{2}$	17,387.90
Lead not ascertained.....			
Gross value of ore.....			\$32,643.34
Less freight to St. Louis, \$8.50 per ton.....			2,256.20
Value received by seller.....			\$30,387.14
Expenses:			
Freight to St. Louis.....		\$2,256.20	
Switching, at 20c. per ton.....		53.08	
Unloading, at 20c. per ton.....		53.08	
Sampling, at \$1.00 per ton.....		265.50	
Assaying.....		60.00	
Purchasing expenses.....		300.00	2,987.86
Cost of 471,138 lbs. dry ore at St. Louis....			33,375.00
Treatment for bismuth, \$33.67 per ton....			7,931.58
Freight on 437,991 lbs. tailings to smelter..			464.15
Treatment charges on same.....			2,097.91

Total expenditures..... 43,868.64

Receipts from Smelter:

For silver, 17,284.80 oz. at 55 cc.....	\$9,506.64
For gold, 243.83 oz. at \$20.00.....	4,876.60
For lead, 20,872 lbs. at 3c.....	626.16
	15,009.40

Cost of 23,403 lbs. bismuth, 123.3c. per lb. 28,859.24
Paid for 22,436 lbs. bismuth, 77.5c. per lb. 17,387.90

23,403 lbs. bismuth extracted at 49c per lb. \$11,471.34

The cost of extraction was 49c. per pound of bismuth.

Since the market price of bismuth was 1.85, there was a gross profit of 61.7c. per pound of bismuth, equal to \$14,419.65 on the lot.

Table VII gives a full account of the cost of treatment of a large lot of 6.26 per cent ore, which may be

considered typical for the average bismuth ores mined in Leadville, Colo. In examining the table, it will be observed that 1410.20 ounces silver and 12.52 ounces of gold were lost in the transaction, while \$626.16 were obtained for 20,872 pounds of lead for which no money was paid to the mine. Taking these three values together, the account stands, \$15,255.44 paid out against \$15,009.40 received, which is a minus of \$246.04 on the lot. Out of the 29,503 pounds which is equivalent to 6.26 per cent bismuth contained in the ore by analysis, only 22,436 pounds were paid for, the difference of 7,067 pounds, equal to $1\frac{1}{2}$ per cent. bismuth, having been deducted to compensate for treatment charges. But 23,403 pounds of bismuth were extracted from the lot. This amounts to only 4.97%. The tailings were carefully analyzed and a score of analyses proved them to contain from 0.25 to 0.35 per cent of bismuth. There was no material loss in working and there were no errors in analyses, to the best of my judgment. The only conclusion remained that the average samples by which the ore was bought did not represent the true average, but showed more bismuth than the ore actually obtained.

The weight of the tailings, namely 437,991 pounds, would seem high, but it must be considered that iron and alumina were rendered insoluble by roasting and that the weight was increased by the flue

ashes in the roasting furnace. They also contained some sediment from the refuse liquors from chlorine stills which were used in place of sulphuric acid, 60° Bé., and were calculated at the value of free acid contained in them.

In the calculation given in Table VII, no charge is made for interest on capital invested, insurance and devaluation on the plant, but the gross profit made on the lot would seem sufficiently high to justify even an expensive plant, including labor-saving machinery, provided a regular supply of ore and a steady market for bismuth can be arranged.

The plant was in successful operation for more than a year. Then all of a sudden the bismuth ores in the mines were reported exhausted. The plant burned down and was not rebuilt. Later on I was told that bismuth ores were mined the same as before but that they were taken up by the smelters and that the bismuth was wasted.

There is no tariff on bismuth, neither is there any duty on bismuth ore. One-third of a million dollars annually go to England which might be kept in this country if bismuth metal and bismuth ores were properly protected by tariff. Bismuth ore is one of the natural resources of the United States and, in my opinion, our Government should see that it is not wasted.

(Continued in the next number.)

SCIENTIFIC SOCIETIES.

DEMONSTRATIONS OF THE BUREAU OF MINES AT THE ARSENAL GROUNDS, PITTSBURG, AND AT THE EXPERIMENTAL MINE OF THE BUREAU NEAR BRUCETON, PA., OCTOBER 30, 1911.

PROGRAM.

At the Arsenal Grounds, 40th and Butler Streets, beginning at 9.00 A.M., October 30, 1911, and closing at 12 M. a demonstration of the work of the Bureau with exhibit of detonation of permissible and other explosives, in the steel-lined gallery, filled with dust and gas.

Exhibits and tests of mine safety lamps in lamp gallery; of electric sparks in gallery No. 2 in the presence of inflammable mixture of air and gas; of training in rescue work with oxygen helmets; of investigations and tests of explosives.

Views of smokeless combustion of coal.

Briquetting of coal and lignite, etc.

Actual explosion at the experimental mine of the Bureau of Mines at Wallace Station, near Bruceton, Pa. Train leaves B. & O. R. R. depot, Pittsburg, at 1.45 P.M. and, returning, leaves Wallace Station at 3.47. This mine has been opened and equipped by the Bureau of Mines with instruments for recording pressures, speed of travel of detonation wave, with various equipment for the making of actual mine explosions due to gas and dust and their observation and study; also of conducting tests of coal-cutting machines, gasoline motor, electric motor and

other mine locomotives, and apparatus under working conditions within a mine.

Demonstration under the joint auspices of the American Red Cross, Pittsburg Coal Operators' Association, and the United Mine Workers of America. The demonstration under the management of the United States Bureau of Mines. Parade of miners under the auspices of the United Mine Workers of America.

At 9.00 A.M., October 31st at Forbes Field (Pittsburg), Pa., an exhibit of skill in first aid to the injured by teams of five miners from various coal operations in the United States, five separate events to be exhibited.

At 11.00 A.M. demonstration by the Bureau of Mines in steel-lined mine gallery 200 feet long, of a permissible shot, followed by an explosion of black powder detonated in the presence of coal dust, with a resulting explosion of coal dust ignited by the non-permissible explosive.

Demonstration of rescue work: men equipped with oxygen helmets will enter the gallery stair still filled with smoke and poisonous gases, will bring out injured men, and give them artificial respiration and first aid.

Demonstration in dangerous practices within gaseous or dusty mines.

At 12 M., President W. H. Taft will deliver souvenir prizes to participants. Short addresses by the Presi-

dent, Governor J. K. Tener, of Pennsylvania, Secretary Walter L. Fisher, of the Department of the Interior, and others.

At 1.00 P.M. the President proceeds to the river front to review marine parade in honor of the Centenary of Opening Navigation on the Ohio River.

Parade of miners will proceed from Forbes Field down Fifth Avenue to a reserved reviewing stand on the river front, passing, en route, in review of President Taft and accompanying officials.

THE DETERMINATION OF NITROGEN IN COMMERCIAL AMMONIATES OF HIGH NITROGEN CONTENT.

Second Report of the Committee on Nitrogen, Division of Fertilizer Chemists, American Chemical Society.

The attention of this committee was recently called to the fact that the determination of nitrogen by the Official Kjeldahl or Gunning method modified for nitrates in commercial nitrate of soda, does not always give concordant results in the hands of different analysts even if the samples in question are presumably identical, as truly representative samples of the same lot of goods. It was thought advisable, therefore, to ask for co-operative work on the analysis of a carefully prepared sample. The

SUMMARY OF ANALYSES OF NITRATE OF SODA.

Averages only are given.

An- alyst.	Moisture. Per cent.	Nitrogen. Per cent.	
1	1.20	15.50	Official Gunning Method, approximately 3 hrs. digestion after adding potassium sulphate.
2	1.64	15.18	Moisture at 100°, 5 gm. 3 hrs., 2 gm. 12 hrs. Modified Kjeldahl Method.
	..	15.30	Modified Gunning Method.
3	1.55	15.60	Official Gunning Method. Moisture at 98-99°C.
4	1.64	15.79	Moisture at 130° C. Used 0.25 gm. and let stand for 5-6 hrs. before heating.
5	1.67	15.33	Modified Kjeldahl Method.
	..	15.22	Modified Gunning Method.
6	0.69	15.48	Official Kjeldahl Method. 2 gm. salicylic acid, 30 cc. H ₂ SO ₄ , 2 gm. Zn dust and Hg. Heated 3 hrs. 1/2 gm. material used. KMnO ₄ added at completion of digestion.
	..	15.55	Comb. Kjeldahl-Gunning Method 2 gm. salicylic acid 30 cc. H ₂ SO ₄ , 2 gm. Zn, Hg and K ₂ SO ₄ . Heated 2 hrs. 1/2 gm. material used. 2 gm. material used for moisture. Dried 7 hrs. 100-102°, C. in air bath.
7	1.24	15.09	Official Gunning Method, modified to include nitrates.
8	1.67	15.25	Official Gunning Method. Moisture at 130° C.
9	2.46	15.48	Stood over night with salicylic acid mixture before digestion.
10	1.98	15.43	Official Gunning Method.
11	0.32 ¹	14.60 ¹	Official Kjeldahl Method.
12	1.63	15.41	
13	1.40	15.45	Modified Kjeldahl-Gunning Method, allowing to stand 1/2 hr. before reduction, and 6 hrs. longer before digestion.
14	..	15.45	Official Gunning Method, modified to include nitrates. Kept mixture very cold with constant shaking for 30 minutes.
	..	15.46	1/2 cc. of water added acid mixture and digested without shaking.
15	..	15.18	1/2 gm. material used and modified Kjeldahl Method, adding 30 cc. acid with 2 gm. salicylic acid dissolved in same
	..	15.29	1/2 gm. material used, adding salicylic acid dry to nitrates.
	..	15.48	1/4 gm. adding wet mixture, salicylic acid and sulphuric acid.
	..	15.62	Dry salicylic acid and mixing with nitrates, using 1/4 gm.
Mean,	1.56	15.41	
Max.,	2.46	15.79	
Min.,	0.69	15.09	

¹ Omitted from average.

letter of instructions sent with the sample substantially requested that nitrogen be determined thereon by the Official Gunning or Kjeldahl methods modified for nitrates as given in *Bulletin* 107 of the Bureau of Chemistry and that moisture be determined on two gram portions of the sample. The reason for specifying two gram portions was that the samples sent out had to be small, as the time available before the summer meeting was limited.

For the same reason, the amount of work asked for was limited so that it represented but a small addition to the routine work of those laboratories to which samples and requests for work were sent. These included state fertilizer inspection laboratories, commercial laboratories and fertilizer manufacturers' laboratories.

Replies were received from 14 out of 22 analysts to whom requests and samples were sent.

The results of the work are briefly shown in the preceding table.

COMMENTS OF THE ANALYSTS.

1. There is a tendency to higher results in using 0.25 gram than when using larger quantities.

4. After quoting illustrations from his own practice in which differences between his laboratory and others range from 0.5 per cent. to 2.0 per cent. of nitrogen were developed, this analyst adds:

"We find that the more nitrogen the goods contain, the longer the digestion is required to stand before heating. We usually put it on in the afternoon and let it stand all night."

14. "We cannot seem to get as high results with 0.5 gram materials as with 0.25 gram, especially so when we add the mixture of salicylic acid dissolved in sulphuric acid."

There is a wide range in the results reported by the various analysts in the results on moisture as well as on nitrogen. This variation does not seem to depend on any one particular factor. The details as reported vary widely as shown in the table and no definite conclusions can be formed from this preliminary work. Local conditions of manipulation and reagents are probably responsible for as much variation as any other factor.

The committee recommends that the study of this subject be continued with a view towards the establishment of a standard sample in sufficient quantity to serve the needs of the members in this division or at least of those members who are particularly interested in this subject.

Respectfully submitted,

Committee on Nitrogen,

C. H. JONES,

F. C. ATKINSON,

F. L. PARKER, JR.,

PAUL RUDNICK, Chairman.

REPORT OF THE COMMITTEE ON PHOSPHATE ROCK.

JUNE MEETING, A. C. S., 1911.

The committee appointed as the Committee on Phosphate Rock, for the better handling of the prob-

lems involved, was divided into three sub-committees on Moisture, Phosphoric Acid and Iron and Alumina, respectively. Each respective sub-committee drafted tentative methods and secured some results during the latter part of last year. Profiting by these results the methods were revised and during the month of April last, these revised methods together with carefully prepared uniform samples were sent out by the committee as a whole for coöperative work. Fifty commercial and consulting chemists were invited to coöperate, and of these, thirty-five signified their desire to assist in the work. Up to the time when this report was compiled results had been received from twenty different analysts. It has been deemed advisable to reject certain results due to their too wide variation from the average and inasmuch as this report is to be considered merely as one of progress, we shall refer to the different analysts by number instead of by name.

The following are the reports of the different sub-committees:

REPORT OF THE SUB-COMMITTEE ON MOISTURE.

The Sub-Committee on Moisture sent out four separate methods for the coöperative work on the work on the determination of moisture. The results reported are shown on the accompanying Table A.

In Method I the determinations were made at the temperature of boiling water, determination A being dried to constant weight, B for five hours.

In Method II the determinations were made at a temperature of 105° C., determination A being dried to constant weight, B for four hours.

In Method III the determinations were made in a vacuum oven with not more than 50 mm. of pressure and at a temperature of 60° C., determination A being dried to constant weight, B for one hour.

In Method IV the determinations were made in an oven ranging between 100 and 105° for five hours.

The variations in the results do not seem excessive for commercial work but the low moisture content makes the percentage variation quite high. The conclusions of the sub-committee are to the effect that it has not been found practical to do satisfactory coöperative work on the sample. The moisture content of commercial phosphate rock is so low that it is not considered advisable to attempt to work out and recommend any special method for its determination. Methods devised for similar materials of higher moisture content will undoubtedly prove satisfactory or at least adaptable to phosphate rock.

Inasmuch as the variations between the averages of different analysts were fully as great in any one method as the variations of the same analyst by different methods, there seemed to be no advantage in attempting to average or otherwise summarize the results of this table.

REPORT OF THE SUB-COMMITTEE ON PHOSPHORIC ACID.

The methods formulated by the Sub-Committee on Phosphoric Acid included three methods of solution, namely digestion with (1) nitro-hydrochloric acid, (2) nitro-hydrochloric acid with sulphuric acid, and (3)

hydrochloric acid alone. The method of precipitation was substantially that given in the official methods of the A. O. A. C. as given in *Bulletin* 107, Bureau of Chemistry, p. 3, with two variations, (A) in which the precipitation of the ammonium magnesium phosphate was made at room temperature and allowed to stand over night, and (B) in which the precipitation was made in ice-cold solution and allowed to stand at a low temperature for two hours. The results received in time to be embodied in this report are shown in the accompanying Table B.

The average results of individual analysts show no material differences in the effectiveness of the three methods of solution tried, except that Method 3, in which hydrochloric acid alone was used for solution, apparently tends towards lower results than the other two methods.

We believe that the most satisfactory way to test the efficiency of any method of solution is to determine the phosphoric acid left undissolved. Since the residue from 5 grams or more of rock can be used for this purpose, the small quantity of phosphoric acid remaining makes it possible to determine much smaller difference than by analyzing the solution made from the rock.

The two different methods of precipitation do not show any definite tendency in one direction or another. Special attention is called, however, to the excellent results obtained by Analyst 3, following the method regularly used in his laboratory, *i. e.*, precipitation of the phosphomolybdate in nearly boiling solution and speedy filtration of both phosphomolybdate and magnesium ammonium phosphate. The method commends itself for technical work on account of its rapidity and deserves further trial. The work of Analyst 10 using the volumetric molybdate method, precipitating cold, also deserves special attention. His results differ from the other volumetric results in being lower and nearer the average obtained by the gravimetric method.

In the hands of Analyst 10 at least, this modification of the Pemberton method gives apparently more satisfactory results than the original Pemberton method as shown in the results of Analyst 13, and is apparently excellently adapted for routine factory control work where rapidity is at least as important as extreme accuracy, if not more so.

When the averages of all the results included in the tabulation are considered, the difference between the different methods of solution and of precipitation almost disappear and the results become, for all practical purposes, almost identical. This points strongly to the conclusion that the variations between individual analysts are due largely to differences in technique and in familiarity with the methods in question.

The suitability of the three solutions for the determination of phosphoric acid must be considered by itself. Although the averages are in good agreement it appears that there is a wider range in individual results from the solution obtained by Method 2, *aqua regia* and sulphuric acid, than secured with solutions prepared by the other two methods. Method 1,

TABLE A.—DETERMINATION OF MOISTURE.

Analyst.	Method 1.		Method 2.		Method 3.		Method 4.		Moisture by methods.
	A. Const. wt.	B. 5 hrs.	A. Const. wt.	B. 4 hrs.	A. Const. wt.	B. 1 hr.	5 hrs.	Const. wt.	
2A.....									4 hrs. Const. wt. 0.50 0.51 0.49 0.50 5 hrs. 0.50 0.50 0.48 0.54 4 hrs. 0.61 0.61 5 hrs. 0.57 0.53
2B.....									
3.....		0.31 0.29							
4.....	0.67	0.65	0.67	0.66			0.66		
5.....							0.59 0.61		
6.....		0.54					0.63		
8.....									0.69 } 0.66 } <i>c</i> 0.65 } 0.65 } 0.65 } <i>d</i> 0.72 } 0.75 } <i>f</i> 0.74 } 0.70 } 0.70 } <i>g</i> 0.70 } 0.71 } <i>h</i> 0.70 } 0.69 } <i>i</i> 0.67 } 0.70 } <i>j</i> 0.69 }
9.....							0.71 0.73 0.67		
10.....			0.71	0.64 _u			0.65		
11.....							0.25 0.25 0.24		0.28 } 0.28 } <i>k</i> 0.34 }
12.....	0.38 } 0.34 } <i>l</i>	0.30 0.35	0.36 0.40	0.45 0.45			0.46 0.43	0.50 0.38	
15.....									0.46 } <i>m</i> 0.47 } 0.50 _n
17.....									
18.....	0.62 _o	0.61	0.78 _o	0.75					
20.....	0.56 } 0.56 } 0.55 } <i>p</i> 0.56 }		0.65 } 0.67 } 0.66 } <i>q</i> 0.67 }				0.60 } 0.61 } 0.61 } <i>q</i> 0.63 }		
21.....	0.49 } 0.52 } <i>l</i>	0.45 _u 0.44 _r	0.52 _r 0.55 _r	0.52 _r 0.59 _r					0.50 } <i>v</i> 0.55 }

b Method used conforms to Methods 2 and 4, except that no vacuum was used. Rel. humidity about 50 per cent. or over. 5 grams used. Constant weight obtained in 3 hours.

c Dried on watch glasses to constant weight.

d Dried in 2 oz. tin boxes to constant weight.

e Dried 5 hours in air bath heated by incandescent lamps to 103° C.

f Dried 1 hour at 108° C.

g Dried 1 hour at 103° C.

h Dried 5 hours at 102–107° C.

i Dried 1½ hours at 104–107° C.

j Dried 1 hour at 102–104° C.

k Dried to constant weight on watch glasses in air bath heated by incandescent lamps to 100° C. Constant weight reached in 4 hours.

l Constant weight in 3½–4 hours.

m Water-bath and cooled in air.

n 100° C.

o Constant weight in 3 hours.

p Constant weight in 5 hours.

q Constant weight in 4 hours. Temperature of water-bath 98.5°.

r Constant weight in 4 hours. Temperature of steam bath 96°.

s Dried 5 hours in steam bath at 96°.

t Constant weight in 3 hours.

u Dried 4 hours.

v Dried 5 hours at 100–105° C.

w Constant at end of first hour.

TABLE B.—DETERMINATION OF PHOSPHORIC ACID.

Analyst.	Sol. 1.		Sol. 2.		Sol. 3.		Miscellaneous methods
	A.	B.	A.	B.	A.	B.	
1.....	30.33 30.08 ¹⁸	30.60 30.35 ¹	30.16 30.19 ¹	29.75 29.93 ¹	30.13 30.49 ¹	29.96 30.07 ¹	
2A.....	29.79	29.81	29.19 ¹⁸	30.35	29.20 } ¹⁸ 29.30 }	30.31	
2B.....	29.79 } ¹⁸ 29.67 } 29.57 }	29.57 } ¹⁸ 29.57 } 29.06 }	29.86 30.18 29.68	30.00 30.18 30.13	29.18 } ¹⁸ 29.39 }	29.30 ¹⁸ 29.39 30.31	
3.....	29.90 29.95		29.81 29.79		29.82 29.93		
							30.12 } ² 30.03 } 30.05 } 30.27 ³
4.....	30.23 29.98	30.36	30.29 30.12	29.87	30.20 29.86	29.84	
5.....	30.04 30.05 30.40	30.33 30.33 30.60	30.12 30.17 30.33	29.89 29.96 30.52	29.85 29.77 30.30	29.74 29.71 30.60	
6.....	30.36 30.32	30.57 30.52	30.27 30.24	30.48 30.45	30.24 30.18	30.56 30.51	
7.....	30.39	30.36	30.56	30.60	30.38	30.36	30.49 ¹⁹ 30.50 ²⁰ 30.50 ²¹
8.....	29.87 30.00 30.02	30.27 30.58	29.71 29.85	30.26 30.04	30.21 30.15	30.66 30.63	
9.....	30.14 30.00	29.48 } ¹⁸ 29.44 } 29.96 }	29.80 29.96 29.94	29.46 } ¹⁸ 29.42 } 29.60 }	29.60 29.84 29.96	29.36 29.96 29.94	
10.....	29.98 30.18 30.18 30.23	29.80 29.80 29.80 30.13	30.33 30.33 30.33 30.36	29.80 29.80 29.80 30.13	29.90 29.93 29.93 29.95 29.95 30.00 30.04 30.06 30.08 30.18 30.26 30.28	29.72 29.72 29.72 29.75 29.75 29.77 29.77 29.93 30.00 30.10 30.16 30.18 30.18 30.18 30.23 30.26	30.22 } 30.24 } ⁸ 30.24 } 30.24 } 30.16 } 30.19 } 30.19 } ⁹ 30.19 } 30.21 } 30.23 }
							30.28 } 30.30 } ¹⁰ 30.34 } 30.18 } 30.19 } ¹¹ 30.21 } 30.24 } 30.26 } ¹² 30.28 }
11.....	29.95 30.16 30.13	30.35 30.04 29.85	30.35 30.29 30.30	30.23 30.08	30.42 29.77	30.23 29.72	30.11 } ¹³ 30.14 }
12.....	30.23 30.18	29.94 29.80	30.26 30.28	29.98 29.95	29.82 29.90	29.94 29.82	
13.....							30.92 } 30.85 } ⁴ 30.58 } 30.52 } 30.70 } 30.85 } ⁵ 30.58 } 30.64 } 31.25 } ⁶ 31.40 }
							30.35 } ¹⁶ 30.27 } 30.30 ¹⁷
15.....	29.79	30.26	29.89	30.16	29.98	29.85	
16A.....	30.32 30.28	30.46 30.36	30.50 30.54	30.71 30.67	30.52 30.66	30.69 30.75	
16B.....	30.43 30.34	30.12 30.23	30.31 30.39	30.18 30.29	30.18 30.22	30.18 30.27 30.12	
17.....							30.50 ⁷
18.....	30.05	30.06	30.15	30.17	30.09	30.10	
19.....	29.95	29.98 29.96	29.85	29.76 29.78	29.94	29.96 29.86	30.00 } ¹⁴ 30.03 } 30.03 }
20.....	30.10 29.56 29.95 29.72	29.85 29.54 29.60 30.10	30.15 30.00 30.05 29.87	30.05 29.49 30.18 29.72	29.85 29.90 30.02 29.87	29.74 29.60 29.92 29.98	30.16 } ¹⁵ 30.24 } 30.27 }
Summary of the averages of individual analysts.							
Mean.....	30.09	30.17	30.14	30.15	30.11	30.12	30.30
Maximum.....	30.39	30.56	30.56	30.69	30.59	30.72	30.72
Minimum.....	29.79	29.77	29.78	29.77	29.80	29.75	30.02

- ¹ Washed with distilled water instead of ammonium nitrate solution.
- ² Solution No. 1 used, and method differs only from Method A as follows: "After measuring out and neutralizing the solution at a bright red, then removed from the fire and precipitated with molybdic solution, and allowed to stand for 15 minutes before filtering. After precipitating with the molybdic mixture the precipitate is allowed to stand 2 hours before filtering."
- ³ Method of solution not stated. Kept in the cold over night instead of for 2 hours.
- ⁴ Solution in HCl and HNO₃. Original Pemberton (neutral molybdate) method. Aliquots from same solution.
- ⁵ Solution in HNO₃. Otherwise same as (⁴).
- ⁶ Same solution as in (⁴), but using molybdate solution over one year old. Omitted from average.
- ⁷ Determined by the standard volumetric method.
- ⁸ Volumetric. Cold pptn. Sol. 1.
- ⁹ Weighing yellow pptn. Cold pptn. Sol. 1. Factor 0.0376.
- ¹⁰ Vol. Cold pptn. Sol. 2.
- ¹¹ Weighing yellow pptn. Cold pptn. Sol. 2.
- ¹² Vol. Cold pptn. Sol. 3.
- ¹³ *Bull.* 107, Bureau of Chemistry.
- ¹⁴ Official method, molybdate digested 30 minutes, Mg ppt. filtered after 2 hours.
- ¹⁵ Same as (¹⁴), but Mg ppt. stood over night.
- ¹⁶ Gravimetric method from solution in HCl and HNO₃.
- ¹⁷ Gravimetric from solution in HNO₃.
- ¹⁸ Omitted from average.
- ¹⁹ Sol. 2. Two hours at room temperature.
- ²⁰ Sol. 2. Volumetric.
- ²¹ Sol. 1. Volumetric.

aqua regia alone seems to have a slight advantage over Method 3, hydrochloric acid alone.

We do not feel justified in trying to estimate the true percentage of phosphoric acid in the sample except to say that it is somewhat higher than 30 per cent.

REPORT OF THE SUB-COMMITTEE ON IRON AND ALUMINA.

The Sub-Committee on Iron and Alumina sent out two methods for the determination of the combined oxides, *viz.*, the acetate method and the glaser alcohol method; two methods for the determination of the oxide of alumina alone, *viz.*, the thiosulphate method and the caustic potash method; and one method for the determination of the oxide of iron by use of the Jones reductor and permanganate titration. The results reported are shown on the accompanying Table C.

The work which the committee has done seems to indicate quite clearly that the methods now commonly used, while often, and perhaps generally, giving quite accurate results when carefully executed in accordance with the directions which the committee has given, are nevertheless subject to grave errors, and one is never certain when correct results are obtained. This is especially true of the methods in which the iron and alumina are precipitated and weighed as the phosphate. We have done a great deal of work on these methods in the past three years, results of which may be stated briefly as follows:

In order that the ignited phosphates may contain enough phosphoric acid to form the normal phosphate, it is absolutely necessary that the second precipitation, either in the acetate, glaser, or thiosulphate method, be made in the presence of an excess of phosphoric acid. It is absolutely necessary to make this second precipitation in order that all lime and magnesia may be removed. It is impossible to exactly wash out the excess of phosphoric acid, leaving only the normal iron and alumina phosphates. It is possible, though hardly practicable, to remove by ignition all excess of phosphoric acid from a precipitate of aluminum phosphate without reducing the normal aluminum phosphate. It is difficult, and the results are very uncertain at best, to remove the excess of phosphoric acid from a precipitate of iron phosphate

without reducing, or rather, driving off some of the phosphoric acid from the compound.

It may be that we can finally secure a method of igniting precipitates in which the temperature of ignition is closely controlled, so that the ignited precipitate will not be reduced, on the one hand, or contain an excess of phosphoric acid, on the other. In the meantime, however, it is the opinion that any of the methods based on the ignition of the phosphate is subject to the above-mentioned errors and uncertainties.

The results submitted this year are about on a par with those obtained last year, and in both instances, it would seem they are better than those obtained in years past. This may possibly be due to the more careful statement of the methods. It is evident, however, from the comments of some of the analysts, that these methods are not yet stated in sufficient detail to prevent the analyst from going astray occasionally.

While the results obtained at this time are, as stated, better than those obtained in previous years, they are far from being satisfactory. A difference of from 0.4-0.6 per cent. on iron and alumina when only about 6 per cent. is present seems too large to be considered satisfactory in a standard method on the results of which large sums of money change hands. If the extreme figures in any of the methods are rejected, the results are considerably better, though still wide. Most of the results on ferric oxide are very satisfactory. The results of two analyses differ quite widely from those of the others and indicate incorrect standards or incomplete reduction respectively.

Work is being continued with the view of working out a method which will be free from the sources of error mentioned above. The object is to weigh the iron and alumina as the oxide rather than as the phosphate. One modification of the acetate and glaser alcohol method has been tried successfully, and the only objection to it is that it prolongs unduly the determination.

Among other methods which we have studied we find the molybdate method very promising, and have obtained very accurate, though slightly low, results with it.

TABLE C.—DETERMINATION OF IRON AND ALUMINA.

Analyst.	Acetate.	Results stated as weight of combined phosphates in 1 gram of rock.				Miscellaneous methods.
		Glaser alcohol.	Thiosulphate.	KOH.	Fe ₂ O ₃ .	
1.....	0.0990	0.1008		0.0566	0.0237	
	0.1034	0.0988		0.0520	0.0237	
2A.....	0.1170	0.1100	0.0750	0.0531	0.0255	
	0.1140	0.1120	0.0760			
		0.1068				
2B.....	0.1135	0.1045	0.0700	0.0550	0.0258	
	0.1135		0.0745		0.0258	
					0.0258	
					0.0273	
					0.0258	
					0.0254	
3.....				0.0208 } ¹¹	0.0208	0.0432 } ¹
				0.0207 }	0.0208	0.0433 }
						Fe ₂ O ₃ ²
4.....	0.1021	0.0996	0.0594	0.0636	0.0179 ¹²	0.0234
5 ³	0.1002		0.0662	0.0594	0.0258	
	0.1002		0.0662	0.0628	0.0258	
	0.1008			0.0628		
6.....	0.1031	0.1090				
	0.1028	0.1030				
	0.1026	0.0982				
7.....	0.0954 ¹²	0.0908 ¹²	0.0723	0.0548	0.0205	
			0.0633			
			0.0610			
8.....	0.1033	0.0922 ¹²	0.1034 } ¹²	0.0488 ¹²	0.0240	
	0.1071	0.0980	0.0995 }	0.0564	0.0220	
		0.0990		0.0630	0.0240	
				0.0600		
9.....	0.1020	0.1024	0.0667 }	0.0698		
	0.1019	0.1028	0.0677 }	0.0678		
	0.1017	0.1036	0.0682 } ¹⁰	0.0714		
	0.1012	0.1032	0.0704 }			
			0.0705 }			
10.....	0.0988	0.0980	0.0638			
	0.0996	0.0986	0.0642			
	0.0998	0.0994	0.0651			
			0.0654			
			0.0508 }			
			0.0516 }			
			0.0587 }			
			0.0600 }			
			0.0604 }			
11.....		0.1010				
		0.1010				
12.....	0.1069	0.1006				
	0.1076	0.1006				
	0.1058	0.1012				
13.....		0.0990			0.0215	FePO ₄ + AlPO ₄
		0.0990			0.0215	0.0894 } ⁴
						0.0894 }
14.....	0.1001	0.0958	0.0559	0.0562	0.0238	
	0.1016	0.0956	0.0554	0.0564	0.0229	
			0.0557	0.0532	0.0232	
				0.0558		
15.....		0.1010				Fe ₂ O ₃
		0.0996				0.0206 }
		0.1014				0.0206 }
						0.0203 }
16.....	0.1026	0.1034	0.0621	0.0614	0.0241	
	0.1041	0.1038	0.0627	0.0632	0.0248	
	0.1026				0.0246 }	
					0.0248 }	
17.....				0.0543	0.0214	0.0947 ⁴
					0.0214	
18.....				0.0600		
				0.0610		
20.....	0.1012	0.1024		0.0564 }	0.0168 }	
	0.1020	0.1030		0.0536 }	0.0168 }	
	0.1004	0.1004		0.0556 }	0.0171 }	
	0.1024	0.1020		0.0480 }	0.0165 }	
	0.1024			0.0432 }		
				0.0550 }		
Summary of averages of individual analysts.						
Average.....	0.1040	0.1013	0.0640	0.0585	0.0234	
Maximum.....	0.1135	0.1096	0.0755	0.0697	0.0258	
Minimum.....	0.1004	0.0957	0.0537	0.0531	0.0205	

¹ Acetate method as practiced in this laboratory. Probably calculated to mixed oxids. Omitted from average.² Complete decomposition of rock.

- ³ Suggests that no indicator be used when neutralizing but before adding the NH_4Cl , NH_4HPO_4 , and precipitating agents, as the solution goes to yellow color as it approaches the neutral point and the slight precipitate appears while still alkaline. The indicator is apparently unnecessary.
- ⁴ Oxalate method.
- ⁵ Bichromate method.
- ⁶ Better results by heating 2 hours on water bath instead of $\frac{1}{2}$ hour. Fourth and fifth results omitted from average.
- ⁷ Using sodium thiosulphate, for first precipitation and ammonium hydroxid for second. Precipitates were red.
- ⁸ Same as (7), but precipitates were white.
- ⁹ Reduced with stannous chlorid.
- ¹⁰ The sulphur seemed to separate out in making up the saturated ammonium thiosulphate solution. Sulphur dioxide fumes did not seem to entirely disappear after an hour's boiling. There seemed to be some sulphur left as a residue on the filter paper when the alumina was dissolved back in dilute HCl.
- ¹¹ Probably calculated to the oxid. Omitted from average.
- ¹² Omitted from the average.

For the last two years all of our work has been done on synthetic solutions. As the question immediately to be answered is not one of solution but of accurate determination of the iron and alumina in solution, it is quite clear that a synthetic solution offers the better solutions for the successful study of the problem.

The sub-committee hopes at an early date to send out methods for general coöperation which will be superior to those now in use.

Among those who coöperated in this work, aside from the members of the committee, were the following:

J. E. Breckenridge, American Agricultural Chemical Company, Carteret, New Jersey.

Emily Bresee, Wisconsin Agricultural Experiment Station, Madison, Wisconsin.

L. S. Bushnell, Armour & Company, Kansas City, Kansas.

F. B. Carpenter, Virginia-Carolina Chemical Company, Richmond, Virginia.

A. E. Dorr, Armour Fertilizer Works, Baltimore, Maryland.

G. E. Fisher, Grasselli Chemical Company, Cleveland, Ohio.

W. P. Heath, N. P. Pratt Laboratory, Atlanta, Georgia.

R. Henry, Virginia-Carolina Chemical Company, Richmond, Virginia.

N. W. Hill, Armour & Company, Chicago, Illinois.

A. C. Johnson, Armour Fertilizer Works, Baltimore, Maryland.

McCandless Laboratory, Atlanta, Georgia.

W. D. McNally, Armour & Company, National Stock Yards, St. Clair County, Illinois.

W. C. Moor, Armour & Company, N. Ft. Worth, Texas.

H. C. Moore, Armour Fertilizer Works, Atlanta, Georgia.

R. Neu, Armour Fertilizer Works, Jacksonville, Florida.

Parker Laboratory, Charleston, South Carolina.

J. R. Powell, Armour Glue Works, Chicago, Illinois.

N. P. Pratt Laboratory, Atlanta, Georgia.

Paul Rudnick, Armour & Company, Chicago, Illinois.

O. M. Shedd, Kentucky Agricultural Experiment Station, Lexington, Kentucky.

Stillwell & Gladding, New York, N. Y.

Stillwell Laboratories, New York, N. Y.

W. D. Turner, Armour & Company, Chicago, Illinois.

O. V. T. Urban, American Agricultural Chemical Company, Carteret, New Jersey.

E. P. Verner, Parker Laboratory, Charleston, South Carolina.

Wiley & Hoffman, Baltimore, Maryland.

J. T. Willard, Kansas State Agricultural College, Manhattan, Kansas.

R. C. Wiley, Kansas State Agricultural College, Manhattan, Kansas.

F. W. Woll, Wisconsin Agricultural Experiment Station, Madison, Wisconsin.

Respectfully submitted,

COMMITTEE ON PHOSPHATE ROCK.

Sub-Committee on Moisture:

W. D. RICHARDSON, *Chairman*,

H. K. McCONNELL,

S. W. WILEY.

Sub-Committee on Phosphoric Acid:

S. W. WILEY, *Chairman*,

A. M. PETER,

H. K. McCONNELL.

Sub-Committee on Iron and Aluminum Oxids:

F. P. VEITCH, *Chairman*,

W. D. RICHARDSON,

A. M. PETER,

C. F. HAGEDORN, *Chairman*.

AMERICAN GAS INSTITUTE.

The sixth annual meeting of the institute will be held in St. Louis, Mo., on Wednesday, Thursday and Friday, October 18-20, 1911.

Headquarters will be in the Hotel Jefferson, and the meetings will be in Memorial Hall, 19th and Locust Streets.

PROGRAM.

"Intensive Scrubbing and Condensing of Gas," by L. E. Worthing, Detroit, Mich.

"The Manufacture of Illuminating Gas in By-Product Ovens in the United States," by W. S. Blauvelt, Semet-Solvay Company, Detroit, Mich.

"Report on Verticals at Providence, R. I.," by Carroll Miller, Providence, R. I.

"Report on Verticals at Manchester, N. H.," by W. G. Africa, Manchester, N. H.

"Turbo-Blower," by an engineer with the General Electric Company.

"Production and Market for Sulphate of Ammonia," by an engineer with the New England Gas and Coke Company, Boston, Mass.

"Tar Distillation and Market for its By-Products," by Alan D. Whittaker, Atlanta, Ga.

"Actual Leakage in Unaccounted-for Gas," by J. D. von Maur, St. Louis, Mo.

"District Holders and their Place in a Distribution System," by R. M. Griswald, Denver, Col.

"Flow of Gas in Mains," by J. W. Battin, Detroit, Mich.

"U. S. Government Report on Electrolysis," by S. W. Stratton, Bureau of Standards, Washington, D. C.

"Pacific Coast Conditions," by John A. Britton, San Francisco, Cal.

"Photometric Work," by C. O. Bond, Philadelphia, Pa.

"Cost and Results Obtained from Automobile Delivery," by L. R. Dutton, Wyncote, Pa.

"Valuation of Public Utilities," by H. C. Abell, New York City.

There will also be some interesting Committee Reports, and the Report of the Editors of the Wrinkle Department and Bureau of Information. It is possible that arrangements may be made for a lecture on "Some Recent Developments in Gaseous Combustion."

The Fourth Annual Meeting of the American Institute of Chemical Engineers will be held in Washington, D. C., Wednesday to Friday, December 20-22nd.

A number of important papers on the general subject of patents; the manufacture and testing of explosives, etc., together with a number of other important subjects relating to chemical engineering.

The 59th Annual Meeting of the American Pharmaceutical Association was held in Boston during the week of August 14th, under the presidency of Prof. E. G. Eberle. The following new officers were installed: *President*, J. G. Godling; *First Vice-President*, Wilhelm Bodemann; *Second Vice-President*, Ernest Berger; *Secretary and Editor*, J. H. Beal; *Treasurer*, H. M. Whelpley. The next meeting will be held in Denver, Colo.

The twenty-eighth annual convention of the Association of Official Agricultural Chemists will be held in Washington, D. C., from November 20-22nd.

The Fifth Annual Meeting of the Italian Society for the Advancement of Science will be held in Rome from October 12-18th under the presidency of Prof. G. Ciamician. The section on pure and applied chemistry will meet under the presidency of Prof. E. Paterno.

EDUCATIONAL

Professor Albrecht Kossel, of the University of Heidelberg, to whom was awarded the Nobel prize for his discoveries in medical chemistry, will deliver the annual Herter lectures at Johns Hopkins University this year on October 4th, 5th and 6th.

Professor Raymond C. Benner, of the department of chemistry of the University of Arizona, has associated himself with Professor R. K. Duncan, of the University of Pittsburg, at which place he will make a study of the smoke problem.

Professor Alexander Smith, of Columbia University, has been elected honorary member of The Chemical, Metallurgical and Mining Society of South Africa, and honorary member of the Sociedad Espanola de Fisica y Quimica. (Madrid).

Dr. F. B. Dains has been elected associate professor of organic chemistry at the University of Kansas and has resigned his position of professor of chemistry at Washburn College.

Dr. John B. Ekeley, professor of chemistry at the University of Colorado, has been appointed State Chemist by the Colorado State Board of Health.

Dr. William McPherson, professor of chemistry at Ohio State University, has been elected dean of the new graduate school of that university.

The new Radium Institute was officially opened in London on August 7th. It possesses radium salts of about \$250,000 value.

Professor J. I. D. Hinds, of Peabody College, Nashville, Tenn., has been elected professor of chemistry at Cumberland University.

Dr. Karl Diewonki, a manufacturing chemist has been elected professor of chemistry at the University of Cracow, Poland.

Dr. K. Auer von Welsbach has been elected an active member of the Academy of Sciences in Vienna.

NOTES AND CORRESPONDENCE.

To the Editor of the Journal of Industrial and Engineering Chemistry.

In Mr. Gardner's paper in the September number of THIS JOURNAL he says that in my tests barytes, etc., appeared to accelerate the drying of linseed oil films, and that "the point at issue seems to be whether the inert pigments really have any chemical action

when enveloped in linseed oil." Reference to my brief paper shows that nothing was said about either of these matters, except to call attention to the curves and suggest that more might be known by future study, also to the fact that the effect of pigments "may perhaps" be due to hindering peroxidation, both of which are obvious. The paper is a record,

and until the facts are questioned, there is no "point at issue." Very likely the effects which all pigments have on oil, whether as stimulators or inhibitors of oxidation or any other process, are due to catalytic or contact action; I do not "feel" that, as Mr. Gardner does, but I think it; so we will not quarrel. I think all pigments have some effect on oil, not depending on their fineness but on their chemical qualities; and that it is incorrect to call one inert to oil if it has a noticeable effect on it, whether to retard drying, like gypsum or lampblack, or to hasten the destruction of the film, like CaCO_3 or BaSO_4 . We do not regard spongy platinum, as used in making H_2SO_4 , as an inert substance, although it does not dissolve or undergo a chemical change. All pigments are, by definition, nearly or quite insoluble in oil; PbO and oil form a cement rather than a paint. PbO is considerably soluble in oil; and it is likely (but not certain) that the minute amount of Pb which was found in oil which had been mixed with white lead was from a trace of PbO in the pigment. I can in no other way understand why oil stops dissolving lead when the basic carbonate (containing hydrate) is present in unlimited amount. In practice we add Pb or Mn compounds to white lead paint to make it dry, in about the same amount that we do to other paints; for all practical purposes the quantity of Pb dissolved is of no account. It is the same way with red lead; true red lead does not combine with oil in the way Mr. Gardner describes; that with which he experimented probably contained as much as 20 or 30 per cent. of PbO . Orange lead, which is red lead nearly or quite free from PbO , will remain uncombined with oil for years, and good ordinary red lead made by modern methods will do so for a month or more.

When saying that white lead is alkaline, Mr. Gardner doubtless means basic; lead is not an alkali metal. If he has any evidence, or knows of any, that white lead or zinc saponify oil at ordinary temperatures, he should publish it; it would be new and important; also how 10 per cent. of a chemically inactive substance can hinder saponification. A. H. SABIN.

To the Editor of the Journal of Industrial and Engineering Chemistry.

SIR:

In the July number, 1911, of THIS JOURNAL there is a description by Mr. George P. Meade of a continuous sampler for condenser waters from evaporators. There is an advantage in such an apparatus, it seems to me, for taking samples of condenser water throughout a strike. Where the entrainment is likely to vary much, as in vacuum-pan boiling, it is quite necessary to take a continuous sample or a great many samples throughout the strike, in order to make an accurate determination of the entrained sugar. But this is the only case, I believe, in which an apparatus of this kind is of any especial advantage.

In multiple-effect evaporators the entrainment is usually quite constant, so that a few samples taken intermittently are as of much value as a continuous

sample. There are, moreover, some objections to the use of a sampler of this kind. It is quite as important in determining the loss of sugar to know the amount of water leaving the condenser as to know the percentage of sugar in it, and it is usually necessary to determine this from the temperatures of the water entering and leaving the condenser. In order to do this the temperature of the sample must be taken immediately as it is drawn from the tail-pipe, or a thermometer must be inserted into the pipe. It is also important that the sample of water shall be evaporated and polarized very soon after it is taken since, on account of its being such a dilute solution and warm, the sugar in it will ferment quickly. A continuous sampler may therefore very easily be misused.

In view of these considerations, it seems to me that a short piece of pipe, with two valves or corks on it, which can be used on either the vertical or horizontal part of a tail-pipe, is more generally applicable and more likely to give accurate results than a continuous sampler.

R. S. NORRIS.

HONOLULU, July, 1911.

THE DETERMINATION OF CAMPHOR.

The extensive use of camphor in medicine and the fact that the Pharmacopoeia includes preparations which must contain definite quantities of camphor make it imperative that there should be a reliable method of assay. There have been in vogue for some time procedures depending on the rotation of an alcoholic, benzol, or oil solution and on the loss by evaporation, but they are open to objection, and in certain instances the results might easily be misinterpreted. Artificial camphor is without rotatory power, natural camphor might contain a portion of the levo body, the rotation varies with the strength of the solvent, and fixed oils themselves on heating often undergo loss or gain in weight. These are a few of the reasons which call for a method based on a more substantial foundation.

Camphor, being of ketonic character, forms with hydroxylamin a well defined oxim, $\text{C}_{10}\text{H}_{16}\text{NOH}$, and advantage has been taken of this property in assaying camphor preparations, the procedure being based on Walther's carvone¹ estimation and on the work of Nelson,² who determined in essential oils by the hydroxylamin method a number of ketones including camphor. The procedure is simple and may be applied directly to spirits of camphor. Of the sample 25 cc. are measured into an Erlenmeyer flask of 100 cc. capacity, 2 grams of sodium bicarbonate are added, and then, accurately, from a burette, 35 cc. of a hydroxylamin solution (20 grams $\text{NH}_2\text{OH} \cdot \text{HCl}$ + 30 cc. H_2O + 125 cc. absolute alcohol aldehyde-free). The flask is connected with a reflux condenser, and heated to gentle boiling for two hours; it is then cooled to 25° C., treated with a mixture of 6 cc. hydrochloric acid (1.12 specific gravity + 6 cc. water), transferred to a 500 cc. volumetric flask,

¹ Pharm. Centralhalle, **41**, 613 (1900)

² U. S. Dept. Agr., Bureau of Chemistry, Bull. **137**, p. 186

rinsing out the condenser and flask with water, and finally made up to volume; 50 cc. portions are filtered off and titrated as follows: Methyl orange is added and the mineral acid neutralized with normal alkali, then phenolphthalein is added and the hydroxylamin hydrochlorid titrated with tenth-normal alkali. A blank must be run, using the same amount of hydroxylamin solution and 25 cc. of alcohol to correspond with the spirits of camphor, the difference in titrations representing the hydroxylamin converted into camphor oxim. Each cubic centimeter of tenth-normal sodium hydroxid is equivalent to 0.01509 gram of camphor.

H. C. FULLER.

U. S. DEPARTMENT OF AGRICULTURE,
BUREAU OF CHEMISTRY

GENERAL NOTES.

Professor Charles L. Parsons, Secretary of the American Chemical Society, has been appointed Chief Chemist of the Mineral Division of the Bureau of Mines, and has been placed in charge of the work in mineral technology.

Professor Parsons will take immediate charge of the investigations along the lines of conservation development and use of the mineral products of the country and make special studies of the processes used in their manufacture.

As soon as the plans for the development of this work are completed headquarters will be established in Washington.

Dr. F. G. Cottrell has resigned his professorship in the University of California in order to accept the position of Physical Chemist with the U. S. Bureau of Mines, with headquarters for the present at the Aston House and Appraiser's Building, San Francisco.

Up to the present time the work of the Bureau of Mines has centered around the coal mining industry, but this year it is beginning in a modest way some work aimed directly at the metalliferous field. Professor Cottrell's work will start with the general fume investigation, but it is felt, in view of the interest of the mining and metallurgical communities, that appropriations will be made later which will make possible the growth and development of work in the metallurgical industry.

Statistics compiled by the United States Geological Survey show that the production of spelter or metallic zinc from ore for the first six months of 1911 was 140,196 short tons, a gain of more than 5,000 tons over half the record output of 1910. Of this production, 5,135 tons was made from foreign ore. Spelter stocks were reduced from 23,232 tons to 17,788 tons. Imports remained about the same but exports were nearly double those of half the preceding year. The apparent consumption of spelter was 135,497 tons, an increase of more than 12,000 tons over the half of 1910 but about the same as in half of 1909. The average price of spelter at St. Louis for the period was 5.36 cents per pound, the London average being 0.2 cent less per pound. During the

latter part of May and the first part of June the average London price was about 0.1 cent higher than the corresponding St. Louis prices. Under this stimulus the May exports of spelter, zinc ore, and dross were largely increased over those of the preceding months.

The Bureau of Standards has recently issued Circular No. 11, entitled "The Standardization of Bomb Calorimeters." It contains some very valuable suggestions and instructions relative to the manipulation of bomb calorimeters and also points out the important features to be considered with respect to the type and construction of bombs, water equivalent, and method of calculating results.

The Bureau is now prepared to furnish standard combustion samples of about 50 grams each of sugar, naphthalene, benzoic acid, etc., accompanied by a certificate giving the heat of combustion of the sample, at \$2 each. They are also prepared to determine the water equivalent of any type of calorimeter including corrections to the accompanying thermometers.

This question is of very great importance, and every chemist who has anything to do with the use of calorimeters should avail himself of the opportunity of at least securing a standard sample and have the thermometers properly standardized.

Cement production in the United States during 1910 has been officially reported upon by Mr. Ernest F. Burchard, of the United States Geological Survey. These figures compared with those for 1909 are as follows:

	Barrels.	
	1909.	1910
Natural and puzzolan.....	1,698,264	1,235,190
Portland.....	64,991,431	75,699,485
Total.....	66,689,715	76,934,675

Prof. James R. Finlay in his report to the State Tax Commission on the Lake Superior copper mines places their total value at \$69,815,000. The Calumet and Hecla mines are appraised at \$31,400,000, and, it is estimated, have a life of twenty years. The tailings dump of this company contains 37,000,000 tons of rich conglomerate sands with a value of \$4,500,000. Six lodes support profitable operations: the Kearsarge, Osceola, Pewabic, Isle Royale and Baltic amygdaloidal beds and the Calumet conglomerate bed. The Lake Superior district stands alone as a low cost producer of copper.

The price of platinum has continued to advance and at present quotations an ounce of the refined metal is worth 2 $\frac{1}{4}$ ounces of gold. Moreover, the tendency is still upward and further advances are expected. Advices from Russia indicate that the present season will see a decrease rather than an increase in the output from the older placers of the Urals.

The Fidelity Chemical Corporation of Houston, Texas, has been incorporated with \$60,000 capital.

stock to erect and run a fertilizer plant in Houston. The officers are: Jas. D. Dawson, *President*; G. O. Haskell, *Vice-President*; R. F. Isbell, *Secretary-Treasurer*.

Dr. D. W. Fetterolf, of Philadelphia, has been commissioned by the U. S. Senate to take charge of the

Chemical Dept. of the U. S. Army Medical Supply Depot in New York City.

Mr. George W. Priest has accepted a position with Messrs. Lloyd & Richards, Inc., as General Manager in their works in Camden, N. J.

BOOK REVIEWS.

Austrian Food Code. Codex Alimentarius Austriacus. 1911. Vol. I, pp. xiv + 461.

This important volume contains definitions, descriptions and specifications for food materials, beverages, and petroleum, together with legislative enactments and similar material, and as a whole is the official source of information regarding the examination and valuation of foods and certain other materials in Austria. A large number of experts have participated in the preparation of material for the codex. The preface is by F. W. Dafert, who is the head of the commission having the work in charge, and there is also an historical introduction explaining the development and extent of the Austrian work with respect to judging of quality and the suppression of adulteration and sophistication of foods and other materials. The present codex is the outgrowth and completion of an enterprise begun under different auspices in 1891 which bore the same title.

C. F. LANGWORTHY.

Materials for Permanent Painting. By MAXIMILIAN TOCH. pp.

208, 4³/₄ × 7³/₄ inches. Price, \$2.00. New York: D. Van Nostrand Company. 1911.

Numerous books treating this subject in some of its aspects have appeared in England and European continental countries, but none recently; and, so far as the reviewer knows, this is the first book on the subject written by a paint manufacturer. Mr. Toch brings to the work a large fund of experience, and ways of looking at the subject which ought to stimulate intelligent thought among those for whose especial benefit it was written. About half the book is given to discussion of some of the more important topics, and the remainder to descriptions of about 150 pigments, with reasons for the author's conclusions as to their merits. If it contained nothing new it would not be valuable; so it is no disparagement to say that not all will agree to everything the author says; but looking at it in a large way, the chief merit of the book is the novel and expert manner in which the subjects are handled.

It is handsomely gotten up and well illustrated.

A. H. SABIN.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

Alcohols. By L. CALVET. 8vo., 376 pp. \$1.50. Ch. Béranger, Paris. (French.)

A Method for the Separation of the Seven Permitted Coal-tar Colors when Occurring in Mixtures. By T. M. PRICE. *Circular* 180, Bureau of Animal Industry.

Analyzed Iron and Steels—Methods of Analysis. *Circular* No. 14, 2nd ed. Bureau of Standards.

Chemistry of the Albuminoids. By O. COHNHEIM. 3d Ed. 8vo. \$3.00. F. Vieweg & Sohn, Brunswick. (German.)

Chemistry for Engineers and Manufacturers. Vol. II. Chemistry of Manufacturing Processes. By B. BLOUNT AND A. G. BLOXAM. 8vo., 530 pp. \$4.00. C. Griffin, London.

Coal, Oil and Gas of the Foxburg Quadrangle, Pennsylvania. By E. W. SHAW AND M. J. MUNN. *Bulletin* 454, U. S. Geological Survey.

Color Mixing Theories and their Practical Application. By KARL MAYER. I. 8vo., 83 pp. \$1.25. J. Springer, Berlin. (German.)

Drying with Air and Steam. By E. HAUSBRAND. 8vo., 142 pp. \$1.25. J. Springer, Berlin. (German.)

Elementary Treatise on Analytical Chemistry. By C. BLAS. Vol. III. 500 pp., 8vo. \$4.25. Gauthier-Villars, Paris. (French.)

Experimental Introduction to Inorganic Chemistry. By H. BILTZ. I. 8vo., 130 pp. \$1.00. Veit & Co., Leipzig. (German.)

Geology and Mineral Resources of the Nizina District, Alaska.

By F. H. MOFFITT AND S. R. CAPPS. *Bulletin* 448, U. S. Geological Survey.

Handbook of Mineral Chemistry. By C. DOELTER. Vol. I. L. 8vo., 160 pp. \$1.50. Th. Steinkopff, Dresden. (German.)

Industrial Chemistry. By H. BLUECHER. Translation. 8vo., 779 pp. \$7.50. Gresham Pub. Co., London.

Introduction to the Chemical Methods of Examination of Food and Food Materials. By H. BAUER. 8vo. \$0.75. F. Enke, Stuttgart. (German.)

Manual of Clinical Diagnosis by Means of Laboratory Methods. By CHARLES E. SIMON. 7th Ed. 8vo., 778 pp. Lea & Febiger, Philadelphia.

Methods of Analysis and Chemical Control for Use in the Factories of the Cuban-American Sugar Co. By GUILFORD L. SPENCER. 8vo., 32 pp. \$1.00. The Cuban-American Sugar Co., New York.

Methods for the Examination of Bituminous Road Materials. By PRÉVOST HUBBARD AND CHARLES S. REEVE. *Bulletin* 38, Office of Public Roads, U. S. Dept. of Agriculture.

Mineral Oils. By H. DELEHAYE. 8vo., 15 pp. \$1.00. Ch. Béranger, Paris. (French.)

Mineral Production of Canada during the Year 1909. By JOHN McLEISH. *Publication* 88, Canada Dept. of Mines.

Mineral Resources of the U. S. for the Year 1909. U. S. Geological Survey.

New Chemical Apparatus Introduced during 1911. By C. POULENC. 8vo., 354 pp. \$0.80. Ballière, Paris. (French.)

- Oil and Gas Fields of the Carnegie Quadrangle, Pennsylvania. By M. J. MUNN. *Bulletin* 456, U. S. Geological Survey.
- Paper Makers' Pocket Book. By J. BEVERIDGE. 2d Ed. 8vo., 211 pp. \$4.00. D. Van Nostrand Co., New York.
- Practical Medical Chemistry. By CHARLES PLATT AND WM. A. PEARSON. 8vo., 260 pp. \$2.50. J. J. McVey, Philadelphia.
- Preliminary Report on Steam Pollution by Mine Waters in Southeastern Kansas. By E. H. S. BAILEY. *Water Supply Paper* 273, U. S. Geological Survey.
- Progress in Tanning Chemistry. By F. C. NEUNER. 8vo., 49 pp. \$0.50. Th. Steinkopff, Dresden. (German.)
- Quality of the Water Supplies of Kansas. By H. N. PARKER. *Water Supply Paper* 273, U. S. Geological Survey.
- Researches on the Electrical Properties of the Alloys of Aluminium. By W. BRONIEWSKI. 8vo., 143 pp. \$1.25. Gauthier-Villars, Paris. (French.)
- Rubber. By PHILIP SCHIDROWITZ. 8vo., 298 pp. \$2.50. Methuen & Co., London.
- Safety Regulations and Devices in Chemical Plants. By K. HARTMANN. L. 8vo., 304 pp. \$4.25. Otto Spamer, Leipzig. (German.)
- Short Introduction to the Internal Construction of Iron-Carbon Alloys. By O. KROENKE. 8vo. \$1.75. Deutsche Verlagsgesellschaft, Berlin. (German.)
- Soda-Potash Salts. By P. MÉKER. 8vo., 245 pp. \$1.25. Ch. Béranger, Paris. (French.)
- Specifications for the Purchase of Fuel Oil for the Government, with Directions for Sampling Oil and Natural Gas. By IRVING C. ALLEN. *Technical Paper* 3, Bureau of Mines.
- Tanning Materials—Leather. By L. JACOMET. 8vo., 249 pp. \$1.25. Ch. Béranger, Paris. (French.)
- The Analysis of Milk and Milk Products. By K. TEICHERT. 8vo., 81 pp. \$0.60. J. Springer, Berlin. (German.)
- Textbook of Analytical Chemistry. By H. WOELBLING. 8vo., 439 pp. \$2.25. Julius Springer, Berlin. (German.)
- Textbook of Chemical Technology. By H. OST. 8vo., \$4.00. M. Jaenecke, Hanover. (German.)
- The Corrosion of Iron and Steel. By J. NEWTON FRIEND. Cr. 8vo., \$1.50. Longmans, Green & Co., New York.
- The Diffusion of Crude Petroleum through Fuller's Earth, with Notes on its Geologic Significance. By J. E. GILPIN AND O. E. BRANSKY. *Bulletin* 475, U. S. Geological Survey.
- The Electrical Section of the Bureau of Mines: Its Purpose and Equipment. By H. H. CLARK. *Technical Paper* 4, Bureau of Mines.
- The Foundations and Results of Chemotherapy. By PAUL EHRLICH. 8vo., 26 pp. Ferdinand Enke, Stuttgart. (German.)
- The Great Cottonseed Industry of the South. By LUTHER A. RANSOM. 8vo., 128 pp. \$1.25. *Oil, Paint and Drug Reporter*, New York.
- The Industrial Application of Water Analyses. By HERMAN STABLER. *Water Supply Paper* 274, U. S. Geological Survey.
- The Manufacture of Chemical Manures. By J. FRITSCH. (Translation.) 8vo., 332 pp. \$2.50. Scott Greenwood & Co., London.
- The Metallurgy of the Common Metals, Gold, Silver, Iron, Copper, Lead and Zinc. By L. S. AUSTIN. 3d Ed. 8vo., 528 pp. \$4.00. Mining & Scientific Press, San Francisco.
- The Negative in Photography. By A. SEYEWETZ. 18°. \$1.00. O. Doin & Fils, Paris. (French.)
- The Nutritive Value of the Non-protein of Feeding Stuffs. By HENRY P. ARMSBY. *Bulletin* 139, Bureau of Animal Industry.
- The Principles of Bleaching and Finishing Cotton. By S. R. TROTMAN. 8vo., 341 pp. \$4.00. Chas. Griffin & Co., London.
- The Rise and Progress of Aerobic Methods of Sewage Disposal. By W. J. DIBDI. Cr. 8vo. \$0.25. The Sanitary Pub. Co., London.
- The Significance of Digestion on Metabolism Considered in Relation to the Newer Investigations in Physiological Chemistry. By E. ABDERHALDEN. 8vo. \$0.50. Urban and Schwarzenberg, Berlin. (German.)
- The Sugar Beet and Beet Sugar. By S. L. JODIDI. 8vo., 94 pp. \$1.00. Beet Sugar Gazette Co., Chicago.
- The Technology of Breadmaking, Including the Chemistry and Analytical and Practical Testing of Wheat, Flour and other Materials Employed in Breadmaking and Confectionery. By W. AND W. C. JAGO. 8vo., 908 pp. \$5.00. 3d Ed. Simpkin, Marshall & Co., London.
- The Use and Care of Mine-Rescue Breathing Apparatus. By JAMES W. PAUL. U. S. Bureau of Mines, *Circular* No. 4.
- Treatise on the Design and Construction of Mill Buildings and other Industrial Plants. By HENRY G. TYRRELL. 8vo., 490 pp. \$4.00. Myron C. Clark Pub. Co., New York.
- Volumetric Analysis. By B. VINAVER. 8vo. \$0.75. Ch. Béranger, Paris. (French.)

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- Determination of Fatty Acids in Soaps and Soap Powders. By G. KNIGGE. *Seifenfabrikant* 1911, No. 31, pp. 773-774.
- Determination of Organic Substances in Water by Means of Permanganate. By H. NOLL. *Zeitschrift fuer angewandte Chemie*, 1911, No. 32, pp. 1509-1518.
- Experimental Sewage Purification at Worcester, Mass. By MATTHEW GAULT. *Engineering Record*, Vol. 64, 1911, No. 9, pp. 242-244.
- Methods of Testing Safety Lamps or other Apparatus for the Detection of Combustible Gases and Vapor. By ARNOLD PHILIP AND T. STENHOUSE, JR. *Journal of the Society of Chemical Industry*, 1911, No. 14, pp. 861-872.
- Methods for the Utilization of Wood Waste. By GEORGE WALKER. *Journal of the Society of Chemical Industry*, 1911, No. 15, pp. 934-936.
- Operating Results at the St. Louis Water Coagulating Work. By GURDON G. BLACK AND WILSON F. MONTFORT. *Engineering Record*, Vol. 64, 1911, No. 6, pp. 162-164.
- Phosphoric Acid and its Compounds in the Manufacture of Beer. By A. FERNBACH. *Brewer and Maltster*, 1911, No. 7, pp. 299-302.
- Purchasing Oil and Gas by Sample. By IRVING C. ALLEN. *Progressive Age*, 1911, No. 16, pp. 699-700.
- Rubber and Rubber Substitutes. By A. KLAGES. *Zeitschrift fuer angewandte Chemie*, 1911, No. 32, pp. 1505-1509.
- Sewage Purification at the Montmesly Works, Paris, France. By M. MATHIEN. *Engineering Record*, Vol. 64, 1911, No. 8, pp. 218-220.
- The Chemical Nature of Tuberculin. By T. PFEIFFER. *Wiener klinische Wochenschrift*, Aug. 3, 1911.
- The Chemistry of Reinforced Concrete. By ED. DONATH. *Zeitschrift fuer angewandte Chemie*, 1911, No. 30, pp. 1398-1402.
- The Employment of the Electrometric Method for the Estimation of the Acidity of Tan Liquors. By J. T. WOOD, H. J. S. SAND AND D. J. LAW. Part II. *Journal of the Society of Chemical Industry*, 1911, No. 14, pp. 872-877.
- The Fusing and Evaporation of Our So-called Highly Fire-proof Materials. By OTTO RUFF AND OTTO GOECKE. *Zeitschrift fuer angewandte Chemie*, 1911, No. 31, pp. 1459-1465.
- The Operation of the Milwaukee Garbage Incinerator. By S. H. GREELEY, L. E. REBER AND E. B. NORRIS. *Engineering Record*, Vol. 64, 1911, No. 7, pp. 186-188.
- The Valuation of Barley in Relation to the Expected Yield from the Malt. By C. J. LINTNER. *Zeitschrift fuer angewandte Chemie*, 1911, No. 33, pp. 1561-1564.

RECENT INVENTIONS.

Reported by C. L. Parker, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Process for the Production of Reaction in Gases.

U. S. Patent No. 991,174.

This invention is a process for the production of reactions in gases by means of electric arcs and consists in the provision of means whereby, in the production of such reactions, a polyphase current, without restriction as to the number of phases, can be

Fig. 1.

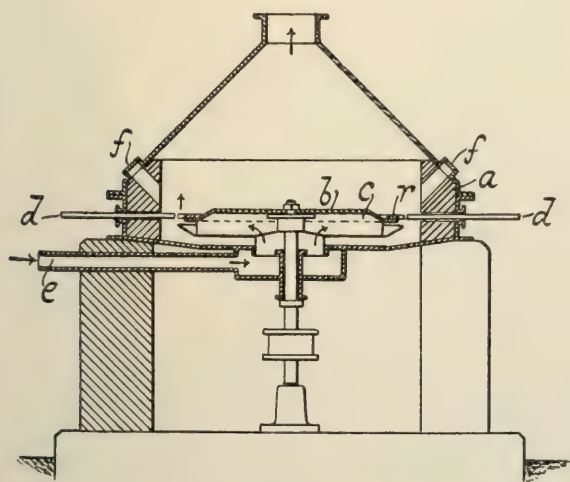
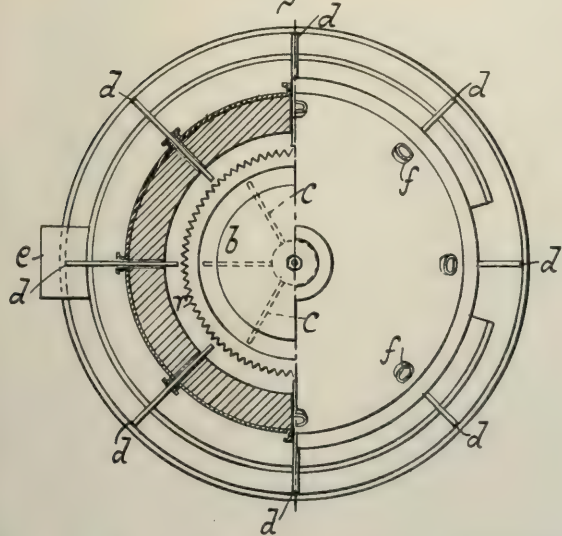


Fig. 2.



used in an electric furnace in such a manner that large quantities of electric energy can be utilized in a simple manner in one furnace and without employing a magnetic field in the furnace to spread out the arcs.

According to the invention electric arcs are caused to spring between a rotating electrode and stationary, but adjustable, electrodes and the gases are made to spread out the arcs so that they cover the whole, or nearly the whole, of the space between the circumference of the rotating electrode and the stationary electrodes, thus compelling the whole, or practically the whole, of the gases which are drawn through the apparatus to pass through and be subjected to the action of the arcs.

a represents the wall of the furnace which is lined with fire-proof material and inside which the circular disc-electrode *b* is mounted centrally so as to be capable of rotation. This rota-

table electrode is provided with radial wings, *c*, and is also provided with a circumferential ring, *z*, which is detachable and can therefore be removed and replaced by a fresh one when desirable. This ring is toothed on the outside as shown. Stationary electrodes, *d*, which must be well insulated, are introduced through the wall of the furnace in the same horizontal plane as that of the electrode *b*, and can be adjusted with regard to the rotating electrode. *e* represents the channel through which the gas supply passes into the apparatus and the arrows indicate the course in which the gases have to travel. The holes marked *f*, which are covered with glass or other transparent material, render it possible to see the ends of the electrodes *d* when setting the same.

The small sectional view shows the positions of the arcs when they are spread out by causing the inner circular electrode *b*

Fig. 3.

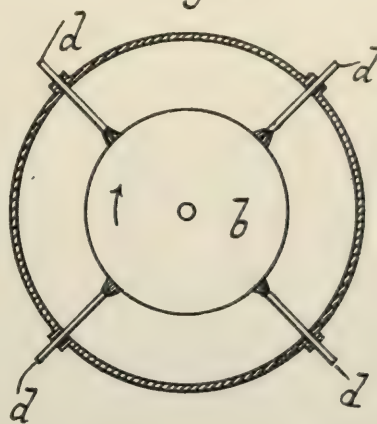
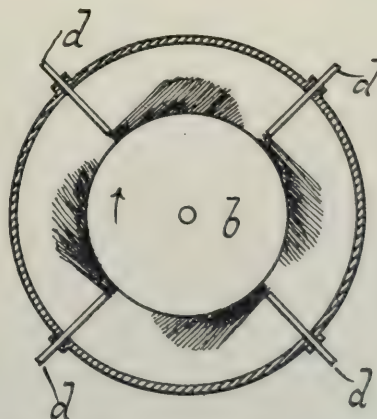


Fig. 4.



to rotate rapidly. The conditions thus produced are favorable for reaction in the gases, as the arcs present a very large surface with which all the gases are compelled to come into contact.

The inventors are Otto Schonherr and Johannes Hessberger, of Ludwigshafen-on-the-Rhine, Germany, assignors to Badische Anilin & Soda Fabrik, of Ludwigshafen-on-the-Rhine, Germany, a corporation of Germany.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF SEPT.

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

Organic Chemicals.

Acetanilid.....Lb.	20 ¹ / ₂ @	23
Acetone (drums).....Lb.	14 ¹ / ₈ @	16 ¹ / ₂
Alcohol, grain (188 proof).....Gal.	2.50 @	2.54
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	3.15 @	3.25
Acetic Acid.....C.	1.69 @	2.39
Aniline Oil.....Lb.	11 ¹ / ₂ @	11 ³ / ₄
Benzoic Acid.....Oz.	11 ¹ / ₄ @	12
Carbon Tetrachloride (drums).....Lb.	7 ³ / ₄ @	8 ¹ / ₄
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (drums).....Lb.	14 ¹ / ₂ @	15 ¹ / ₆
Citric Acid (domestic).....Lb.	38 ¹ / ₂ @	39
Camphor (refined in bulk).....Lb.		45
Dextrine (imported potato).....Lb.	5 ¹ / ₂ @	7
Dextrine (corn).....C.	2.79 ¹ / ₂ @	2.95
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 ¹ / ₂ @	9 ¹ / ₂
Glycerine (dynamite).....Lb.	18 ³ / ₈ @	20
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7 @	7 ³ / ₈
Pyr gallic Acid (bulk).....Lb.	1.25 @	1.55
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	2.02 ¹ / ₂ @	2.18 ¹ / ₂
Starch (potato).....Lb.	3 ³ / ₈ @	4 ¹ / ₄
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 ⁷ / ₈ @	5 ¹ / ₄
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	30 ¹ / ₄ @	30 ³ / ₄

Inorganic Chemicals.

Acetate of Lime (gray).....C.	1.87 ¹ / ₂ @	1.92 ¹ / ₂
Acetate of Lead (brown, broken).....Lb.	7 ³ / ₄ @	8
Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (drums) 16°.....Lb.	2 ¹ / ₂ @	3 ¹ / ₄
Ammonium Chloride, gray.....Lb.	6 @	6 ¹ / ₄
Arsenic, white.....Lb.	1 ⁷ / ₈ @	2 ¹ / ₃
Ammonium Carbonate, domestic.....Lb.	8 @	8 ³ / ₈
Aluminum Sulphate.....Lb.	90 @	1 ³ / ₄
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 ¹ / ₄
Barium Nitrate.....Lb.	5 ¹ / ₂ @	6 ¹ / ₄
Borax, crystals (bags).....Lb.	3 ¹ / ₂ @	4
Boric Acid, crystals.....Lb.	7 @	7 ¹ / ₂
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.26 ¹ / ₄ @	1.35
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	94 @	96
Chalk (light precipitated).....Lb.	4 ¹ / ₂ @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (bags).....C.	60 @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 ¹ / ₄ @	8 ¹ / ₂
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	85 @	88
Nitric Acid, 36°.....Lb.	3 ⁷ / ₈ @	4 ¹ / ₄
Nitric Acid, 42°.....Lb.	4 ⁷ / ₈ @	5 ¹ / ₄
Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25

Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 ³ / ₈ @	10 ³ / ₄
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals.....Lb.	8 ¹ / ₄ @	9 ¹ / ₂
Potassium Nitrate (crude).....Lb.	4 ¹ / ₈ @	4 ⁷ / ₈
Potassium Bichromate, 50°.....Lb.	7 ³ / ₈ @	7 ³ / ₄
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	66 ¹ / ₂ @	69
Salt Cake (glass-makers).....Lb.	57 ¹ / ₂ @	67 ¹ / ₂
Silver Nitrate.....Oz.	33 ¹ / ₂ @	36
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 ¹ / ₄ @	5
Sodium Chlorate.....Lb.	8 ¹ / ₄ @	9 ¹ / ₂
Sodium Bicarbonate (English).....Lb.	2 ³ / ₄ @	3
Sodium Bichromate.....Lb.	5 ⁵ / ₈ @	5 ² / ₄
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 ¹ / ₂
Sodium Hydroxide, 60 per cent.....C.	1.80 @	1.85
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.		8
Sodium Nitrate, 95 per cent., spot.....C.		2.22 ¹ / ₄
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 ³ / ₄ @	10
Strontium Nitrate.....Lb.	7 ¹ / ₄ @	8
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	85 @	1.00
Talc (American).....Ton	15.00 @	20.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	11 @	12 ¹ / ₄
Tin Oxide.....Lb.	45 @	47
Tin Chloride (36°).....Lb.	11 @	11 ¹ / ₂
Zinc Chloride (granulated).....Lb.	4 ¹ / ₂ @	4 ² / ₄
Zinc Sulphate.....Lb.	2 ¹ / ₄ @	2 ¹ / ₂

Oils, Waxes, Etc.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 ¹ / ₄
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	9 @	20
Corn Oil.....C.	6.37 ¹ / ₂ @	6.42 ¹ / ₂
Cottonseed Oil (crude), f. o. b. mill.....Gal.	35 ³ / ₄ @	37 ¹ / ₈
Cylinder Oil (light, filtered).....Gal.	19 ¹ / ₂ @	20
Japan Wax.....Lb.	8 ³ / ₄ @	9
Lard Oil (prime winter).....Gal.	77 @	80
Linseed Oil (raw, city).....Gal.	83 @	84
Linseed Oil (double-boiled).....Gal.	90 @	91
Paraffine Oil (high viscosity).....Gal.	23 ¹ / ₂ @	24
Paraffine (crude 120 @ 122 m. p.).....Lb.	3 @	3 ¹ / ₄
Paraffine (refined, domestic) 120 @ 122 m. p.....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Rosin Oil (first run).....Gal.	— @	37 ¹ / ₂
Spindle Oil, No. 1.....Gal.	14 @	14 ¹ / ₂
Stearic Acid (double-pressed).....Lb.	8 ³ / ₄ @	9
Sperm Oil (bleached winter) 38°.....Gal.	76 @	78
Tallow (acidless).....Gal.	63 @	66
Tar Oil (distilled).....Gal.	30 @	31

Metals.

Aluminum [No. 1 ingots].....Lb.	19 ³ / ₄ @	20
Antimony (Hallet's).....Lb.	— @	—
Bismuth.....Lb.	— @	1.80
Copper (electrolytic).....Lb.	12.30 @	12.35
Copper (lake).....Lb.	12 ⁵ / ₈ @	12 ³ / ₄
Lead, N. Y.....Lb.	— @	4.50
Nickel.....Lb.	40 @	50
Platinum (refined).....Oz.	— @	45.00
Silver.....Oz.	52 ³ / ₄ @	53
Tin.....Lb.	— @	41 ¹ / ₄
Zinc.....Lb.	— @	5.90

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EDITORIALS.

FACILITIES FOR INDUSTRIAL RESEARCH.

Much has been said and written of late about men qualified by training and experience to conduct industrial research, but what would seem to be a matter of equal, or even greater importance, is the question of the *facilities* available for the study and solution of these industrial problems.

Industrial Research is the great basic principle upon which we develop our manufacturing and engineering industries. The results of this research must not only precede the establishment of manufacturing enterprises, but such study must continually accompany, supervise and direct any manufacturing operations which assume to be intelligently managed.

Makeshift solutions and "fixing" will keep a plant going for a time, but the final result of such unscientific management is cumulative and leads to a condition requiring drastic action, usually in the form of reorganization, refinancing or insolvent liquidation.

The list of manufacturing plants which have been led to oblivion by footless management is long, and is still growing. We have all seen perfectly good manufacturing enterprises slowly crowded out of the competitive field while other concerns with equal, but no greater commercial advantages in the identical line of manufacture, prospered. A careful examination into the basic causes of the failing concerns will usually disclose a "tinkering" and unscientific policy, or no policy at all, in the study and solution of factory problems.

Managers who would submit every point involving a question of law to their attorney regardless of cost, and act strictly within his instructions in reaching a decision, will pump barrels of expensive compounds into their boilers without a particle of knowledge as to its probable action or effectiveness; will adopt new oils or lubricating solutions for their costly machinery without knowing anything about their value for the purpose intended; or will buy a formula or a "secret mixture" to make ashes burn, all on the strength of an advertisement, a "scientific" article in a subsidized press, or on the "advice" of a salesman.

There are times when the whole future of a business depends upon selecting the right process, method or machine to prepare a piece of work. Some managers, however, will be contented under such a stress to render a "snap" decision; others will make a few "cut and try" experiments; others will spend much money to find out what the "other fellow" is doing or using, or send a man to Europe to pick up a few ideas.

On the other hand, the concerns with the scientific

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foundation and scientific habits of thought and management develop with assurance and permanence. Their products have sound scientific merit. They may be said to be "lucky" in the purchase of new inventions, or "audacious" in the adoption of improved processes of manufacture. As a matter of fact, however, their "luck" and "audaciousness" consists in having the knowledge of what is scientifically correct, and in having the courage of their scientific convictions. If the chemistry, physics and mathematics involved in their steps forward is right, their "luck" is right. If the fundamental principles underlying the manufacturing problem or product considered are not stable, the structure erected upon them is likely to be shaky.

The daily problem of the factory manager or the engineering enterprise must be met and solved by the application of scientific knowledge if the work is expected to endure. Some of these problems may be solved from fundamental facts, which are a part of the general knowledge of experienced engineers. The theory may be used in a great many cases, but it is difficult to make it answer all questions. For example, we may calculate the flow of a perfect liquid through a frictionless pipe, or a pipe with a known coefficient of friction, but this formula will not give the answer to the factory superintendent who wants to know how much mucilage, or similar viscous solution, he may pump through a thousand feet of 2 in. lap welded gas pipe in July and how much in January. The data for establishing such a simple calculation as this is not available, and experimental observations are necessary to give the correct answer before work can proceed.

Another class of problem involves facts which can only be established by experiments, observations and conclusions based upon a study of the whole proposition from the standpoint of its *proposed application*.

How are the facts—the foundation-forming facts—upon which the industrial manager is to build his process, develop his products, determine his business policy, or render his decision in important matters to be obtained? Obviously, on the simpler and better understood problems, the factory manager may consult experts who have made a special study of this particular field. This expert advice is limited to tried-out problems, and the number of such experts equipped with facilities to conduct experimental investigations, are very few when compared with the broad fields covered by the industries.

Several large corporations have developed their own experts and their own laboratories, but these are not only special in their equipment and experience, but are not available to outsiders.

The most logical method for the study of a factory problem would then be to undertake its solution in a laboratory especially equipped with the standard appliances for executing industrial operations, and provided with all the means for the prompt, proper and accurate determination of experimental data,

in a way and on a scale which would make this data available for factory application.

Many of our industrial managers have found it more profitable to devote their energies and resources to the maintenance of high tariffs, the elimination of competition, or the control of raw material supply, than to the perfection of process and product through scientific research. All of their researches have been political and sociological rather than scientific, and it is a serious commentary on conditions when we must acknowledge that they have usually made it pay big dividends.

The lure of large and quick profits in the field of "political research" has attracted so many researchers that it is being overworked. The public is taking an interest in developments along this line, and is now demanding a scientific and equitable basis for tariff, for raw material distribution, and for quality and value in products. As these tendencies take form, the manufacturer will find himself confronted with problems of efficiency in handling, manufacturing and marketing his materials and in the quality and merit of his product.

The development of industrial research would apparently be a logical means of alienating American manufacture from the "tinkering" manager, the patrons of fake science, the victim of sales talk, the patent fiend, the crumbling tariff walls, the exploiter of politics and people, and innumerable other dangers. Furthermore, as the pressure of domestic and foreign competition becomes a factor of increasing importance, the prompt appreciation and utilization of all scientific and engineering progress becomes a matter of self-preservation.

A great scholar once said to me that he did not see "why it takes so much expensive apparatus and equipment to do chemical research work now, when some of the most brilliant work in former years had been done with cigar boxes, a few glass bottles, and other homely inexpensive appliances."

In the early days of the West great mines were discovered and developed from a "grub-stake" of one hundred dollars, or even less. These surface claims were soon all located, and the future development of our mineral resources required the investment of large sums of money, but this did not prove to be an obstacle to their development, nor a reason for the abandonment of good prospects. Machinery had to be installed, shafts sunk, and tunnels run in barren ground in order to prospect ore bodies not easily accessible; but money was always found to finance these researches. It would be interesting to know what the mineral resources of this country would now be had the development been confined to that within the reach of a one hundred-dollar "grub-stake" or the "burro" method of transportation.

As the day of surface discovery in mining quickly passed, and the mineral development required more knowledge, and a substantial outlay for prospecting and tools to work with, so the day of glass bottles and cigar box research in the field of applied chemistry

is passing, and we need resources with which to carry our investigations into the new fields.

It is true that Priestley, Lavoisier, Liebig, Rumford, all produced classic researches without expensive laboratories or equipments. Yet a careful inventory of the resources and appliances available to some of these scholars will bear a striking similarity to the equipment of some of the present-day laboratories attempting research. Chemical laboratory development has not kept pace with the development of the science itself and the progressive difficulties of the problems to be undertaken. The so-called modern laboratory for research bears a strong resemblance to the arena in an obstacle race. Young men unselfishly offer their service in the fields of research, often at great sacrifices to themselves and others dependent upon them, only to find that they are obliged to waste their time hurdling the obstacles of meagre equipment and inadequate facilities.

Researches are often either entirely abandoned, or limited to a narrow field through lack of simple appliances, or competent mechanical assistance. Other demonstrations give negative or misleading results through improperly constructed apparatus or because there is not a mechanic with a suitable tool equipment available to build needed parts, or to make the necessary rearrangements. Research men are trained in *inefficiency* by being compelled to use makeshift and "junky" apparatus, and also by being compelled to do work which could be done better and at less cost by others.

The laboratory requirements for industrial study are no more exacting, expensive, or difficult to develop than those of mechanical, electrical or metallurgical engineering. The chief difference between chemical engineering laboratories and those of the other engineering subjects seems to be that we chemists have not developed our facilities while other engineers have kept pace with the advancement of their respective industries.

The writer recently visited a number of the leading engineering schools and industrial establishments in Europe for the purpose of observing their equipment and comparing it with that provided for similar work in this country. Mechanical, metallurgical, electrical and chemical engineering laboratories were examined with equal care, in Charlottenburg, Dresden, Munich, Freiburg, Zurich, London, Manchester and other places. Mechanical laboratories were invariably provided with steam engines, compound Corliss engines, turbines, pumps, gas engines, pro-

ducer gas sets, Diesel oil engines, and a long list of standard mechanical engineering appliances, equipped with instruments for observing, measuring and recording data. Metallurgical laboratories contained every facility for making, testing and studying alloys. At Freiburg the government smelters, mines and ore-dressing establishments are used for both study and instruction. Electrical engineering equipment always includes every type and kind of modern machine for generating, measuring and using electricity. But laboratories do not seem to exist where chemical students and investigators may study the applications of physics and chemistry to fundamental industrial operations as other engineers are studying the applications of their fundamentals in mechanical, electrical, and metallurgical fields.

Researches can not be undertaken which involve single and multiple effect distillation, evaporation, filtration, calcination, condensation, absorption, drying, controlled temperature reactions, vacuum and special atmosphere reactions, etc., except on a test tube or beaker scale.

It is the purpose of a large portion of this Society to further the interests of Industrial Chemistry. We are all vitally interested in its aims and purposes. There are many suggestions for ways and means of accomplishing something in this great field.

We might establish scholarships and encourage young men to study chemistry; grant funds to promote special research; accumulate reference libraries; suggest to the teachers courses of training better adapted to produce the class of men needed in Industrial Chemistry; there are many ways in which the support and influence of this Society might profitably be directed.

But there is one field which is richer in the promise of results than all others combined; a field which will yield a more immediate, direct, and tangible return to our own industry, our own profession, and to our own members; and that is in *recognizing the necessity of systematic study of industrial problems and throwing the undivided influence of this Society into the establishment and maintenance of laboratories equipped to answer the eternal questions arising as a result of industrial progress*. Laboratories to solve problems and establish facts, not from the standpoint of fundamental theories and principles involved, which presumably have been established by the test tube and beaker method but to *solve problems from the standpoint of their proposed application*.

ORIGINAL PAPERS.

TRANSFORMATION OF OTHER FORMS OF CARBON INTO GRAPHITE.

By W. C. ARSEM.

Received Oct. 1, 1911.

INTRODUCTION.

The conditions under which "Amorphous carbon" is transformed into graphite have been the subject of much discussion, and many statements have found

their way into the literature which are not supported by experimental evidence. The following theories are commonly held:

1. A high temperature alone will convert "amorphous carbon" into graphite (Moissan).
2. Pure carbon is not converted to graphite by heat alone (Berthelot).
3. Graphite is the result of intermediate formation

and decomposition of carbides, due to the presence of mineral matter as an original constituent, or purposely added (Acheson).

I have collected all available references relating to this problem and have given briefly the evidence in favor of each theory.

Despretz¹ heated several varieties of carbon in an arc. He states that "any carbon which is submitted for a long time to a high temperature becomes proportionately softer. Finally it is transformed into graphite." No physical or chemical tests for graphite are described.

Berthelot² was first to recognize the ambiguity in the use of the term graphite, and proposed the Brodie test as a criterion.

He was not able to convert amorphous carbon to graphite at a *white heat* in hydrogen. A retort carbon rod which had been ignited, thrust into a stream of oxygen, and quenched in water when fully incandescent, was found to have been graphitized on the tip.

WORK OF MOISSAN.³

Moissan heated in the arc furnace different varieties of carbon enclosed in carbon crucibles, and after heating determined their specific gravity and their behavior toward nitric acid and potassium chlorate. He found that the products differed in specific gravity, but in all cases they yielded yellow graphitic acid with the oxidizing mixture. He concluded that heat alone will convert "amorphous carbon" into graphite. His results are given in the following table:

TABLE 1.

Carbon.	Ash after firing. Per cent.	Specific gravity after firing.
Sugar carbon.....	0.11	2.19
Carbon from Al_4C_3	2.11
Cryst. graphite from cast iron, 1150°.....	1.30	2.17
Cryst. graphite from cast iron, 1150°, high temperature.....	0.17	2.18
Cryst. graphite from cast iron cooled in water.....	1.29	2.16
Graphite from cast iron by silicon.....	0.85	2.20
Graphite from platinum.....	1.10	2.06-2.18

He showed also that graphite separates during the cooling of a saturated solution of carbon in various metals and that graphitic carbon is a product of the decomposition of many carbides, but gives no specific gravity determinations except for Fe and Al.

WORK OF ACHESON.

Acheson noted the formation of graphite by the decomposition of silicon carbide at high temperatures. He also noted that the furnace core of bituminous coal coke in the carborundum furnace became converted, to a considerable extent, into graphite. The following statements, made by Acheson, are to be found in the literature and in patents:

(a) The amount of graphite produced by highly heating pure carbon is insignificant and impracticable, but if the carbon is mixed with considerable mineral matter the yield of graphite is enormously increased. (U. S. Patent, 568,323, Sept. 29, 1896.)

(b) A mixture of 97 parts coke, or charcoal, and 3 per cent. iron oxide, can be changed, to a greater or less extent, into graphite by varying the time and temperature of heating. As the iron is insufficient to convert all the carbon to carbide, it is assumed to have a catalytic effect, first forming a carbide which decomposes, yielding graphite and setting free iron, which again forms carbide, and the cycle is repeated. (U. S. Patent, 617,979, Jan. 17, 1899.)

(c) A natural variety of carbon containing mineral matter, such as anthracite coal with 5.783 per cent. ash, gives practically pure graphite with 0.033 per cent. ash. This result is assumed to be due to the intimate admixture of "inherent impurities," it being stated that even with the best artificial mixing and distribution of carbon and mineral matter, the conversion to graphite will be more or less irregular and incomplete. (U. S. Patent 645,285, March 13, 1900.)

(d) Petroleum coke, to which has been added 5 per cent. iron in the form of oxide, is heated to the vaporizing point of iron in a specially constructed electric furnace. The iron vapor is stated to cause conversion of the petroleum coke to graphite. (U. S. Patent 711,031, October 14, 1902.)

(e) Acheson also makes the following statements in an article presented before the Franklin Institute.⁴

1. "Comparatively pure petroleum coke produces practically no graphite.

2. "Impure bituminous coal coke produces large quantities.

3. "The larger the known percentage of impurities in the bituminous coal coke, the greater the amount produced.

4. "Only a part of the core in the carborundum furnace (bituminous coal coke) is converted into graphite, this not being increased even by repeated use of the same grains in successive carborundum furnaces." He concludes: "The amount of graphite produced in the core of the carborundum furnace, and also in graphite articles I have made, is much too great to be accounted for by the theory that it is formed by the dissolution of the fixed carbides formed by the contained impurities, and carbon sufficient to satisfy the chemical formula. The most probable and satisfactory explanation is that a catalytic action occurs—a progressive formation and dissolution of carbides. The temperature being much above the point of volatilization of silica and all other possible impurities, a rapid dissipation of the active agents takes place, and it is completed in this case before the conversion of all the amorphous carbon can occur."

No experimental evidence is given by Acheson to show that pure carbon is not graphitized by simple heating. Direct proof is also lacking to show that a small amount of mineral matter can cause, or facilitate, the conversion of a large amount of carbon to graphite.

The only experiment bearing on this point that I could find described in the literature was in an article by F. A. J. Fitzgerald,⁵ from which I quote as follows:

¹ *Compt. rend.*, **29**, 709-24.

² *Ann. chim. phys.*, **19**, series 3, 392.

³ "Le Four Électrique."

⁴ *J. Frank. Inst.*, **147**, 475, 486.

⁵ *Ibid.*, **154**, 338.

"Two carbon rods, one composed of very pure lampblack carbon, and containing less than 0.2 per cent. ash, the other made of petroleum coke carbon which had been intimately mixed with a certain amount of ferric oxide, were heated side by side in an electric furnace. At the end of the experiment, the rod that had contained the iron was found to be graphitic, could be easily cut with a knife, took a beautiful metallic luster on rubbing, and would mark paper like an ordinary pencil.

"The pure carbon rod showed little change, was dull black in color, nearly as hard as before heating, and would not leave a mark on paper. One end of this carbon rod, however, was clearly graphite, from the fact that it had been exposed to the action of carbide-forming elements. These vapors had even penetrated to a certain depth in the carbon rod, and in so far as this had occurred the rod showed a brilliant graphitic appearance, was soft, etc."

This experiment would seem to be inconclusive, because two different varieties of carbon were employed, one being heated with iron oxide and the other without. It should have been determined whether or not pure petroleum coke is graphitized when heated without admixture with iron oxide.

Borchers¹ claims that a small amount of Al or Al₂O₃ can convert a considerable quantity of amorphous carbon to graphite.

He does not state what kind of amorphous carbon is used or what happens if this carbon be heated without addition of mineral matter, but refers to work by Borchers and Mögenburg ("Graphit aus Amorpher Kohler in Borchers' Institut für Metallhüttenwesen und Elektrometallurgie") which was not available.

Borchers¹ claims priority for the theory that graphite is produced from amorphous carbon by the formation and decomposition of carbides, on the basis of an article in *Zeit. f. Elektrochem.*, 3, 394 (Mar. 20, 1897), from which he quotes:

"Metals which form carbides, alloys, or more or less dissociable compounds, can assist the crystallization of carbon." The article mentioned was a discussion of methods for the production of the diamond, no reference being made to graphite in this connection.

Moreover, Moissan² had previously prepared graphite by crystallization of carbon from solution in metals and by decomposition of many carbides.

Other patents relating to the manufacture of graphite are:

E. G. Acheson, 542,982, July 23, 1895. Purifies carbon by volatilizing impurities in an electric furnace.

H. Y. Castner, 572,472, December 1, 1896. Heats rods of retort carbon or other carbon by current. Product has lower density and greater conductivity.

Herbert H. Wing, 598,549, February 8, 1898. Amorphous carbon converted into graphite by prolonged heating at high temperature. (Ordinary coke mentioned.)

DEFINITION OF GRAPHITE.

Much confusion has arisen from the uncertainty as to the exact significance of the term "graphite." Many different varieties of graphite have been described, and widely differing values for the various physical constants have been published.

Berthelot was the first to adopt the Brodie¹ test as a criterion. He defined graphite as any variety of carbon which yields graphitic oxide when oxidized with nitric acid and potassium chlorate. Moissan seems to have felt the need of a further criterion, as he defined graphite as a variety of carbon, usually crystalline, having a specific gravity about 2.2, which yields graphitic acid when oxidized.

Some of the uncertainty has been removed by the recent work of Le Chatelier and Wologdine.² They showed that a number of natural graphites, when freed from mineral matter and air, had practically the same specific gravity, 2.255, this value being also obtained for a sample of Acheson graphite.

Charpy³ considers the density a much better criterion than the Brodie test.

My own work indicates that any variety of carbon, after heating to 3000°, will give a green or yellow oxidation product by the Brodie test, although many samples have a relatively low specific gravity and lack the physical characteristics of graphite. There is no proof that the yellow oxidation product has the same composition in every case. It may be that a variety of structurally related oxidation-products may exist.

It was found, however, on examination of a large number of carbon samples, that the graphitic properties become more pronounced as the specific gravity approaches 2.26. We have then either a series of carbons of varying molecular complexity, the end member being graphite, or a series of mixtures of graphite with other forms of carbon. In either case it seems to me that there can be little objection to the following definition:

Graphite is that allotropic form of carbon having a specific gravity of 2.25 to 2.26.

Those varieties of carbon which have some of the physical properties of graphite, such as color, softness, and streak, but a lower specific gravity, may perhaps be regarded as impure graphites; that is to say, mixtures of graphite with other forms of carbon.

PURPOSE OF THE INVESTIGATION.

The points at issue are the following:

1. Can a pure form of carbon be transformed into graphite by simply heating to a high temperature?
2. If this is not the case, is it possible to cause this transformation to occur by heating the carbon, well mixed with a quantity of mineral matter, *insufficient to form carbides* from all the carbon present?

There are two ways of attacking the problem:

- (a) To determine the effect of heating various forms of pure carbon alone and with small amounts of added mineral matter.

¹ B. C. Brodie, *Liebig's Ann.*, 114, 7, 1860.

² *Compt. rend.*, 146, 49 (1908).

³ *Ibid.*, 148, 920 (1909).

¹ *Elektrometallurgie*, third edition, 564 (1903).

² *Ann. Phys. Chem.*, [7] 8, 466 (1896).

(b) To remove the mineral matter from certain varieties of impure carbon, which ordinarily change to graphite when heated, and see if the change will still occur.

Both methods were tried.

EXPERIMENTAL METHODS.

All samples were ground to fine powder before firing, to facilitate the determination of specific gravity, and all samples were tested, after firing, by treatment with potassium chlorate and nitric acid.

Grinding.—To insure freedom from enclosed air which would vitiate the specific gravity results, all samples of carbon were ground in a roller-mill. This is a steel cylinder with a tightly fitting cover on each end, and contains four steel rolls. All the surfaces are case-hardened and polished, to insure a minimum of wear. As to the extent to which iron is introduced, it was found that after 50 hours' grinding of a 20-gram sample of petroleum coke, the ash had increased only 0.09 per cent. The mill is rotated at 200 r. p. m., and from two to eight hours is sufficient to grind most substances, so that the largest particles are not over 0.005 mm. in diameter.

Firing.—The samples were packed in small Acheson graphite crucibles with tightly fitting covers. These, in turn, were placed in larger tubular graphite crucibles, closed at both ends, the space between the smaller and larger crucibles being packed with Acheson granular graphite, previously fired and containing only mere traces of ash. The samples thus protected were fired at approximately 3000 to 3300° C., in an experimental tube furnace for 15 minutes. This furnace consists of a heater tube of Acheson graphite surrounded by an insulated carbon tube with an annular free space between them. The outer carbon tube

is well packed in granular petroleum coke, but no packing material is in contact with the heater. With the exception of the graphite heater tube, which was renewed for each run, the furnace has been used for a great many runs and is practically free from metallic impurities.

When making tests of purified and unpurified samples of the same kind of carbon, the purified samples were always fired in a tube which had not previously been used for firing impure carbon.

Specific Gravity.—Specific gravity determinations were made on samples pulverized as above stated, using a pyknometer of the form shown in sketch holding about 7 cc. The sample was weighed in the pyknometer, which was then half-filled with Kahl-

baum's C. P. benzene, and heated to the boiling point of the benzene to remove air and fill the pores of the carbon. Owing to the fineness of the powder, this can be accomplished in a few minutes. The pyknometer was then cooled to 20° C., filled to the mark with benzene, and weighed. Results are referred to water at 4° C. The limit of accuracy is about 0.005.

BRODIE'S TEST.

All samples before and after firing were tested by Brodie's method, which consists in heating the sample with fuming nitric acid and potassium chlorate. "Amorphous carbon" is converted into brown soluble substances, while graphite is changed to green graphitic oxide, or yellow graphitic acid, according to the concentration of the nitric acid, or the duration of the treatment.

In my experiments I used in some cases nitric acid, distilled from a mixture of concentrated nitric and sulphuric acids. In other cases the nitric acid was made by distilling well-dried potassium nitrate with concentrated sulphuric acid, as recommended by Moissan.

EXPERIMENTAL RESULTS.

Petroleum Coke.—This was obtained from the Standard Oil Company, in lump form, and contained 0.10 per cent. ash. These lumps, when fired, had all the physical properties of graphite, being soft, and of a silver-gray color. They marked paper easily. A sample of this graphite, pulverized before firing, had, after firing, a specific gravity of 2.26. This value was checked a number of times. A sample of the coke ground with 5 per cent. ferric oxide had a specific gravity after firing, of only 2.22.

It is thus seen that quite pure petroleum coke, when fired without additions, yields a very good grade of graphite, and that the addition of iron oxide is, if anything, disadvantageous.

Bituminous Coal Coke.—This was ordinary foundry coke, containing about 10 per cent. of red ash, mostly iron, and silica.

Lumps of this coke, when fired, became bright gray, and gave the characteristic gray streak on paper. This material seemed harder than petroleum coke graphite. Some of the powdered coke, when fired, had a specific gravity of 2.192.

A sample of unfired coke was treated with fused sodium hydroxide, then with water, and finally with hydrochloric acid. The ash was now reduced to 5.70. After firing, its specific gravity was 2.225.

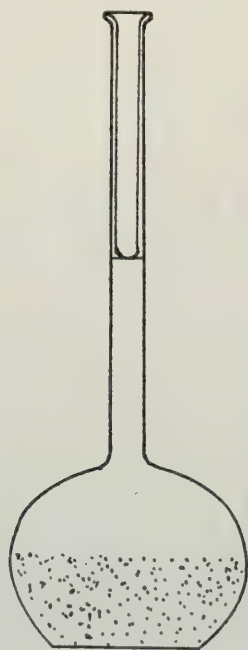
The results of these experiments are given in Table No. 2.

TABLE 2.

	Ash before firing.	Ash after firing.	Specific gravity after firing
Crude coke.....	10.00	2.07	2.192
Treated with fused NaOH, then with HCl.....	5.70	0.78	2.225

Here we see again that the smaller the amount of mineral matter present, the higher the specific gravity reached on firing.

Anthracite Coal.—A sample of Lackawanna coal,



Pyknometer.

Transformation of other forms of carbon into graphite.

containing 6.46 per cent. ash, when fired in lump form came out bright gray, rather hard, and with a tendency to cleave into plates and angular fragments like the unfired coal. It marked paper with some difficulty, and its feel and appearance were much less graphitic than in the case of the fired foundry coke and petroleum coke.

A pulverized sample, when fired, had a specific gravity of 2.133.

Some of the pulverized coal, when treated with fused NaOH, then washed and treated with HCl, had its ash reduced to 0.20 per cent., and this purified coal, when fired, had a specific gravity, of 2.149, a value slightly higher than that given by the crude coal.

To check this result, some samples of coal obtained from the U. S. Geological Survey were treated in the same way. The results were even more striking, as may be seen from Table 3.

TABLE 3.
Results of firing anthracite coal above 3000°.

Coal samples.		Ash before firing.	Sp. gr. after firing.
Lackawanna.....	Crude	6.46	2.133
Lackawanna.....	Purified	0.20	2.149
U. S. G. S. "Buckwheat No. 1"...	Crude	17.68	2.125
U. S. G. S. "Buckwheat No. 1"...	Purified	1.73	2.170
U. S. G. S. "Buckwheat No. 5"...	Crude	13.30	2.138
U. S. G. S. "Buckwheat No. 5"...	Purified	0.93	2.180

Anthracite coal, therefore, is a form of carbon which graphitizes only imperfectly, in spite of the high percentage of ash which is well distributed throughout the material. We have here excellent conditions for catalytic action without a corresponding effect. The results show that the presence of ash *hinders*, rather than *assists* graphitization. Some samples of coal seem to yield purer graphite than others, especially after the ash has been removed.

Lampblack.—A commercial variety of lampblack, known as "Patton's Sun-proof," containing about 0.2 per cent. ash, principally iron oxide, when fired in the tube furnace reaches a specific gravity of 2.090. Some of the lampblack, unfired, was ground with 5 per cent. ferric oxide and fired.* This had a specific gravity of 2.094. Another sample of lampblack was impregnated with ferric oxide so as to obtain as good a distribution as possible in the following way:

The lampblack was stirred into a solution of ferric chloride and ammonia was added to precipitate ferric hydrate, when the lampblack precipitated with the ferric hydrate, forming an apparent homogeneous mixture. This mixture was well dried and divided into two portions; the first was heated one hour *in vacuo* at 1600° and the other one hour at 2000°, to reduce the iron oxide to metal, and then both were fired in the graphite tube furnace at about 3300°. After firing, the specific gravity of the first portion was 2.122, and of the second portion 2.109. All these fired samples were indistinguishable from each other by physical or chemical tests. We have here a pure form of carbon which reaches a limiting density of about 2.10, and this limit is not appreciably raised by the presence of even 5 per cent. ferric oxide, al-

though the distribution of the latter was about as perfect as possible and the conditions especially favorable for a catalytic transformation into a more graphitic variety of carbon if this were possible. They are all grayish black, non-crystalline powders. They all yield by Brodie's test, a yellow graphitic acid but have none of the characteristic properties of graphite.

Another sample of lampblack, Reichard's No. 7, was also fired, and reached a density of 2.074.

Patton's Sun-proof lampblack was also heated with small percentages of different substance, but no catalytic effect was noticeable.

The results are summarized in the table:

	Sp. gr. after firing.
Patton's L. B., 0.2 per cent. ash.....	2.090
Patton's L. B., 5 per cent. Fe ₂ O ₃ ground together.....	2.094
Patton's L. B., 5 per cent. Fe ₂ O ₃ by pptn. (a).....	2.122
Patton's L. B., 5 per cent. Fe ₂ O ₃ by pptn. (b).....	2.109
Patton's L. B., 5 per cent. Al ₂ O ₃	2.080
Patton's L. B., 1 per cent. Si.....	2.076
5 per cent. MnO ₂	2.091
5 per cent. NiO.....	2.099
Reichard's L. B.....	2.074

RETORT CARBON.

The carbon obtained from the inside walls of gas retorts occurs in three varieties, black, gray and white. These differ in ash content and in behavior on heating, and show in a striking way that the ability to graphitize is independent of the amount of ash present. Both the white and the gray varieties yield excellent graphite, although the former is very low in ash and the latter high.

The black variety which is also low in ash does not graphitize but reaches a density of 2.11. Four different substances tried as catalyzers had no effect, the density after firing being practically the same as that of the same carbon fired without mineral additions.

TABLE 4.
Effect of heating retort carbon above 3000°.

	Ash before firing.	Ash after firing.	Sp. gr. after firing.
White retort carbon.....	0.34	0.10	2.265
Gray retort carbon.....	2.66	0.16	2.263
Black retort carbon.....	0.23	0.10	2.110
Black retort carbon, 1 per cent. CaO.....	..	0.31	2.123
1 per cent. SiO ₂	0.12	2.117
1 per cent. Li ₂ CO ₃	0.05	2.120
2 per cent. Fe ₂ O ₃	0.09	2.178

DIAMOND.

Some white diamonds when fired became converted into a coke-like carbon having a specific gravity of 1.915, which does not mark paper.

Parsons and Swinton¹ heated a diamond in the focus of a cathode ray tube at 1890° and state that it was converted into coke. The specific gravity was not stated.

These results are especially interesting since it has been commonly supposed that the diamond is converted into graphite by heat, and statements to that effect appear in most text-books.

CONCLUSIONS.

All the pure forms of carbon which have been tested, when fired above 3000°, reach a limiting density

¹ *Proc. Roy. Soc.*, 80, 184 (1908).

which is not appreciably raised by the addition of small amounts of mineral matter. The end product is graphite in some cases and not in others. Pure petroleum coke, heated without addition of mineral matter, is converted into graphite of excellent quality, while lampblack, although it increases in density, does not reach the value corresponding to graphite, nor acquire any of its other physical properties, even when heated with various oxides.

The impure carbons show a similar behavior. The properties of these carbons after firing are characteristic for each variety of carbon and independent of the amount of ash present.

Anthracite coal is only imperfectly graphitized by heating. The specific gravity of the fired material was approximately the same for three samples having a range of ash content from 6.46 to 17.68 per cent. Moreover, coal from which most of the ash has been previously removed graphitizes better than the crude material.

Bituminous coal coke, which graphitizes fairly well, yields an even better product if a part of its ash has been removed before firing.

It must, therefore, be concluded that a small amount of mineral matter exercises no beneficial effect in the manufacture of graphite by the heating of carbon and that the quality of the product cannot be improved in this way. As to the effect of mineral matter on the rate of conversion, no data are yet available, although some experimental work along this line has been started. At 3000° the maximum density is reached in less than 15 minutes, for any variety of carbon.

We need some theory of the nature of graphite and of amorphous carbon which will permit a rational explanation of the changes which occur on heating. The following discussion is a tentative step in this direction.

THE NATURE OF GRAPHITE.

Graphite in the most restricted sense of the term is an allotropic form of carbon having a definite and perhaps not very complex molecular configuration. The molecule might, for example, be regarded as two benzene rings side by side, and joined at all six angles, the extra bonds being satisfied as in the usual centric formula. Such a formula might be used to explain the formation of mellitic acid and graphitic acid by oxidation of graphite.

AMORPHOUS CARBON.

When an organic compound is decomposed, there results a mixture of substances constantly increasing in complexity until finally carbon is obtained. This carbon need not be regarded as a simple substance, but may be considered to be a mixture of many varieties of carbon each with a different number and arrangement of atoms in the molecule. According to this view it seems better not to regard "amorphous carbon" as the name of a distinct allotropic form, but rather as a general term covering all varieties of carbon except graphite and diamond. In speaking of amorphous carbon, therefore, the source of each sample should be stated.

THE MODE OF TRANSFORMATION.

In a given sample of amorphous carbon, some of the molecules will be capable of easily undergoing rearrangement under the influence of heat to form graphite molecules, while others will not, and the proportion of molecules capable of such change will determine the character of the final product.

Petroleum coke would therefore consist almost wholly of graphitizable molecules, while anthracite coal contains a smaller proportion.

RESEARCH LABORATORY,
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A METHOD OF ANALYZING SOME COMMERCIAL GOLD ALLOYS. METALS PRESENT: GOLD, SILVER, COPPER AND OCCASIONALLY ZINC AND TIN.¹

By JAS. O. HANDY.
Received August 9, 1911.

PREPARATION OF SAMPLE.

Use a sharp file. Remove particles of steel with a magnet. Weigh out 0.5 gram of filings in a 4-ounce beaker. Add 50 cc. of *aqua regia* (40 HCl and 10 HNO₃). Heat just to boiling for 15 minutes or until decomposed. The AgCl is almost all dissolved, when boiled with the strong acid. Boil down to 10 cc., add 25 cc. HCl and again boil down to 10 cc. or until the AgCl begins to separate.

SILVER.

Dilute to 150 cc. with water. Boil until the AgCl coagulates well. Cool, let stand until clear. Filter on a weighed paper, and wash the AgCl. Dry and weigh. ($\text{AgCl} \times 0.7527 = \text{Ag}$)

ZINC.

Add sufficient HCl to the filtrate to make 5 per cent. of concentrated HCl by volume. Pass H₂S through the cold solution rapidly for fifteen minutes. Filter and wash with H₂S water. The filtrate contains only the zinc. Boil off H₂S and precipitate with Na₂CO₃. Boil for fifteen minutes. Filter and wash with hot water. Dry, burn off in porcelain and weigh ZnO after blasting. ($\text{ZnO} \times 0.8034 = \text{Zn}$)

TIN.

For the separation of Sn from Au and Cu in the sulphide precipitate, we take advantage of its solubility in HCl. The precipitate (and filter paper) is placed in a beaker and covered with 50 cc. of a mixture of water (35 cc.) and HCl (15 cc.). Boil for ten minutes. Cool. Filter. Add HCl to make 25 per cent. of concentrated acid by volume. Pass H₂S to reprecipitate any dissolved Cu. Filter and wash with H₂S water. Neutralize filtrate with ammonium hydroxide. Acidify with 1 cc. of HCl. Pass H₂S to precipitate the Sn. Filter. Wash with H₂S water. Burn off in a porcelain crucible, igniting finally over a blast. Weigh SnO₂. ($\text{SnO}_2 \times 0.788 = \text{Sn}$) The CuS recovered as above is converted into CuO and is then dissolved in 5 cc. conc. HNO₃, by warming. Any SnO₂ present is recovered and weighed, the amount being added to that already obtained.

¹ Paper read at the Indianapolis Meeting of the American Chemical Society before the Industrial Section, June 30, 1911.

The Cu solution is added to that recovered from the gold, by the next operation.

COPPER.

Burn off the sulphides of gold and copper in a porcelain crucible, avoiding a heat greater than that required to burn off the filter paper. This hinders the shrinkage of the metallic gold, and leaves it more porous so that the CuO is readily dissolved out. Too high a heat causes CuO to unite with the glaze of the crucible. Place the Au and CuO mixture in a 4-ounce beaker. Add 10 cc. of concentrated HNO₃. Boil for 10 minutes. Add 3 cc. of concentrated H₂SO₄ and boil until the HNO₃ is all expelled, and SO₃ fumes are coming off freely. Cool, add 50 cc. of water and 5 grams of sodium acetate; boil and filter off the gold (the gold residues are weighed as an approximate check and are saved for their commercial value only. Gold is best determined by fire assay). Cool the filtrate and add 5 grams of potassium iodide. Stir until dissolved. Titrate with decinormal hyposulphite of sodium: 1 cc. = 0.0063 gram Cu.

GOLD.

Scorify 0.5 gram of filings with 40 grams of test lead, 1 gram of borax glass and 1 gram of powdered silica. The borax and silica flux are placed on the mixture of alloy filings and test lead. If the lead button resulting from scorification is hard, repeat the scorification, adding 10 grams more test lead and 2 grams of borax and silica flux. Cupel carefully and weigh Au plus Ag.

The determinations previously made make it possible to calculate quite closely the amounts of Au and Ag, etc., in the alloy.

We make up a mixture containing the same metals in approximately the same proportions. 0.5 gram of this "control" mixture is then scorified and cupelled side by side with an equal weight of the alloy. After weighing the gold and silver buttons from the assay and the "control," they are alloyed separately with three parts of pure Ag.

The alloys must be thoroughly melted in order to insure homogeneity. Flatten the buttons by hammering or rolling.

Part with HNO₃ of graded strengths as is the usual assaying practice. Boil well with water, dry, ignite and weigh Au. Deduct Au from Au plus Ag. The difference is Ag. Increase both Au and Ag figures by the amounts of loss shown by the Au and Ag used in the "control" assay. The fire-assay for Au and Ag yields in most chemists' hands the highest and the most accurate results. The correction for fire loss (volatilization) is far higher for Ag than for Au. Gold alloys analyzed by us had the following limits of composition.

	Per cent.
Gold.....	48.0 to 99.50
Silver.....	0.5 to 26.00
Copper.....	0.0 to 18.00
Zinc.....	0.0 to 7.50
Tin.....	0.0 to 2.00

Those alloys highest in Ag were most difficult to dissolve in *aqua regia*.

We found the ratio 1 HNO₃ to 4 HCl most efficient. *Aqua regia* 1 to 3 was less efficient and 1 to 2 very unsatisfactory. Increasing the percentage of HNO₃ in the mixture failed to cause more rapid solution, but increase of HCl produced unexpectedly rapid and complete decomposition.

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CUPELLATION.

By RAYMOND C. BENNER AND MINER L. HAPTMANN
Received September 7, 1911.

In the last few years there have been so many kinds of cupels proposed and placed on the market that it seemed desirable to determine the relative value of some of the best known, regarding silver loss, conditions of surface, etc., after cupellation. These observations suggested the investigation of the properties of substances other than bone ash, for separating lead and silver in the process of cupellation.

In order to obtain uniform and comparative conditions an electrically heated muffle was used for all cupellations in this investigation. The temperature was determined by means of a Le Chatelier platinum iridium pyrometer. Two cupels were run side by side and the pyrometer placed between them about 1/4 inch above the tops of the cupels. The muffle used was just wide enough to take two cupels and allow room for moving them about. The back part of the furnace was always hot enough to "open" the buttons and to start them "driving," after which they were pulled forward near the door of the muffle.

After thorough drying, the cupels were heated in the muffle, at about 800° C. The lead button was dropped into the cupel and the muffle door closed until the lead had melted down and begun to oxidize. The cupels were then pulled to the front of the muffle where the pyrometer registered about 665° C. and continually watched. If any signs were discovered of more litharge being formed than was absorbed, the cupel was pushed back a little. It was found sufficient in many such cases to merely turn the cupel around, so that the colder side would be facing the hotter part of the furnace. When the button had become quite small, seemed to be revolving, and would "blik" in from 2 to 3 minutes, the cupel was pushed back into the furnace where the temperature was from 750° C. to 800° C. This was found necessary on account of a small amount of lead being retained in the silver button if the cupellation were completed at a lower temperature.

The bone ash obtainable for making cupels varies so much in size and purity that some standard was necessary, with which to compare the cupels tested. One was selected which gave the following screen test:

	Per cent.
On 60 mesh.....	0.007
On 80 mesh.....	7.83
On 90 mesh.....	33.22
On 100 mesh.....	8.58
On 120 mesh.....	43.65
Through 120 mesh.....	6.72

This bone ash gave the following losses for silver:

Average.	Lead. Grams.	Silver. Mgs.	Silver loss. Per cent.
Series of six.....	10	35-40	2.45
Series of six.....	10	35-40	2.30
Series of six.....	10	35-40	2.33
			—
		Average.	2.36

Among other brands of bone ash, tests have been made of the following in regard to silver loss:

	Lead. Grams.	Silver. Mgs.	Silver loss. Per cent
D. F. C. Co. X ¹	10	35-45	2.4
D. F. C. Co. XX.....	10	35-40	2.4
D. F. C. Co. XXX.....	10	35-40	2.6
Braun's AAA ²	10	35-40	2.4
Braun's AAAA.....	10	35-45	2.5

The manufacturers state, "Practically 75 per cent. of D. F. C. Co.'s X grade will pass a screen apparatus of 0.0147 inch (approximately 40 mesh), the XXX grade 0.00675 inch (approximately 80 mesh), and the XX grade 0.0091 inch (approximately 60 mesh)." Braun's AAAA grade is rated at 80 mesh, and the AAA grade at 60 mesh.

Silver losses in cupels, made as nearly alike as possible from the standard bone ash and the cupellation carried out under the same conditions, vary as much as 0.2 per cent., and, consequently, the results are accurate only to this degree.

All of the following tests were made under the same conditions as given for bone ash cupels.

Morganite cupels are very hard, both hot and cold, and do not crack. The surface is smooth and fine-textured. They give the smallest silver losses of any which have come to our notice.

No. in series.	Grams of lead.	Mgs. of silver.	Silver loss. Per cent.	Vol. matter. Per cent.	Lead absorbed. Per cent.
6	10	35-45	2.17	0.0	92.0
6	10	35-45	1.82	0.0	..
		Average,	1.99		

Cassette cupels are light gray and hard enough to be handled safely when cold but when heated they become soft and pulverulent. The surface is smooth

ram of losses are given below:

No. in series.	Grams of lead.	Losses are given below:			
		Silver.	Silver loss.	Vol. matter.	Lead absorbed
6	10	35-45 ^f	3.29 ^{cent.}	Per cent.	Per cent.
6	10	35-45	3.29 ^{cent.}	Per cent.	Per cent.
		—	—	5.9	98.1
		Average, 3.09			

Brownite cupels are very similar to cassite in regards physical properties. They are like cassite as in color. The surface is slightly pitted after use. The silver button has a tendency to flatten out at the end of the cupellation. The losses are given out at the

No in series.	Grams of lead.	Mgs. of silver.	Silver loss, Per cent.	Volatile matter, Per cent.
6	10	35-45	2.95	7.1
6	10	35-45	2.83	..
Average, 2.89				

¹ Denver Fire Clay Co., Denver, Colorado.

³ The Braun Corporation, Los Angeles, California.

Cement cupels are used, at present, in some districts. This material affords a very cheap substitute for bone ash and answers fairly well for small amounts of silver. Mixtures of cement and bone ash give better results than neat cement. The cupels are very hard before heating and are sufficiently adherent afterwards to be handled without danger of breaking. The surface is as smooth as a cupel of bone ash and the button is detached with equal ease. Cupels made of Atlas Brand Portland cement gave the following results:

No. in series.	Grams of lead.	Mgs. of silver.	Silver loss. Per cent.
6	10	35-45	3.51
6	10	35-45	3.25
			<hr/>
		Average,	3.38
One-half cement and one-half bone ash.			
6	10	35-45	3.05
6	10	35-45	2.85
			<hr/>
		Average,	2.95

The losses in cement cupels have been determined and compared with those in bone ash cupels by J. W. Merritt.¹ He finds that at orange heat, when using 10 mgs. of silver, 6.38 per cent. of the silver is lost in bone ash cupels and 6.64 per cent. in cement cupels; at light cherry heat, 4.62 per cent. in bone ash, and 4.91 per cent. in cement. The temperatures are not stated in degrees.

T. P. Holt and N. C. Christenson² have made a study of cupels made from different brands of cement as well as mixtures of cement and bone ash. They give the following summary of their results:

SILVER LOSSES AT VARIOUS TEMPERATURES.				
Average temp.	U. S. Portland cement.	Red Devil Portland cement.	Half cement and half bone ash.	Bone ash.
Degrees C.	Per cent.	Per cent.	Per cent.	Per cent.
915	1.30	1.34	1.21	1.26
925	1.81	1.72	1.54	1.70
945	2.53	2.56	2.42	2.42
965	3.37	3.42	3.05	2.96

These temperatures are the temperatures of the lead buttons, which are about 125° C. hotter than the air just above the cupel.

Magnesium oxide or calcined magnesite has been suggested for making cupels. Some difficulty was encountered in finding a suitable binder for the material. Various organic materials were tried which made adherent cupels until they were heated, when they became very pulverulent. Mixtures with Portland cement were used but the cupels became very fragile after heating. Silica was next tried as a binder. Gelatinous silica made from water glass and hydrochloric acid was mixed with the magnesium oxide and fairly hard cupels were made. After cupellation, however, deep cracks were found on the surface of the cupels where lead oxide had been absorbed. Cupels made with varying proportions of sand (60 and 80 mesh) and magnesium oxide were tried, with the results given below:

¹ *Mining and Scientific Press*, May 7, 1910

² *Eng. Min. J.*, 90, 560-1.

MgO. Per cent.	Sand Per cent.	Condi- tion of cupel.	Lead Gms.	Silver Mgs.	Silver loss. Per cent.	Surface.
80	20 coarse	soft	10	35-45	2.5	slightly cracked
80	20 coarse	hard	10	35-45	2.6	slightly cracked
80	20 fine	soft	10	35-45	2.3	deep cracks
80	20 fine	hard	10	35-45	2.5	deep cracks
85	15 coarse	soft	10	35-45	3.2	badly pitted
85	15 coarse	hard	10	35-45	2.2	badly pitted and cracked
85	15 fine	soft	10	35-45	3.3	slightly cracked
85	15 fine	hard	10	35-45	2.5	badly cracked

None of the magnesium oxide cupels have properties either as to loss of silver or as to hardness after cupellation, which warrant the substitution of that substance for other cupel material.

SUMMARY.

Under similar conditions, with about 10 grams of lead and 40 mgs. of silver, the average percentage losses in different cupels were as follows:

	Silver loss. Per cent.
Morganite.....	1.99
Cassite.....	3.09
Brownite.....	2.89
Bone ash.....	2.36
Cement.....	3.38
Equal parts cement and bone ash.....	2.95

It was furthermore determined that cupels made of different grades and sizes of bone ash give the same percentage loss of silver within the limits of experimental error.

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HEAT RADIATION.

By HAROLD P. GURNEY.

Received Aug. 9, 1911.

Heat transmission by radiation is utilized in the abstraction of heat from the zone of combustion in furnaces, and it is the principal restrictive factor in the maintenance of high temperature. Chemical and metallurgical industries abound with instances where application of the well established laws of heat radiation and conduction would reveal important information with regard to economy of operation or design. Although heat radiation is rarely unaccompanied by conduction and convection of heat, it may well be treated separately, at first, as it is subject to different laws.

The laws of heat radiation differ in very essential respects from the laws of heat conduction. Heat always flows from high to low temperature, but the rate of flow of radiant heat is not proportional to the temperature difference. When heat is transmitted by conduction, the thermal pressure causing the flow of heat may be considered as proportional to the absolute temperature, consequently the rate of flow per unit of temperature drop is a constant, because the differential of the thermal pressure with respect to the temperature is a constant. The pressure of radiant heat is proportional to the fourth power of the absolute temperature, consequently the rate of flow per unit of temperature drop at any temperature is proportional to the cube of the absolute temperature.

Heat of conduction flows through solids, its rate of transit depending on the heat-transferring properties of the solid, its density, its specific heat, and its thermometric conductivity. Heat of radiation passes through space between surfaces, its rate of transit depending on the nature and disposition of the surfaces between which it passes and not on the space itself, that is, not on the nature of the gas or vapor filling that space. This is not absolutely correct, as there is no gas which is completely diathermanous, that is, which does not absorb radiant heat; but for air, products of combustion, and most gases of common occurrence, the absorption of radiant heat is negligible over short distances.

The fourth-power law of heat radiation was first advanced by Stefan¹ who found it to accord with the results of experimental researches of Dulong and Petit, de la Provostaye and Desains, and Draper and Tyndall. Boltzmann later demonstrated mathematically from thermodynamic principles that such a law should hold.

A surface of A square feet at a temperature of Θ_1 degrees absolute (equals θ_1 degrees Fahrenheit plus 460.7) radiates R heat units² to another surface whose absolute temperature is Θ_2 in a length of time T hours. The mean solid angle subtended by the latter surface with respect to the surface in question is ϕ hemispheres. The net coefficient of emission and absorption between two surfaces is E . According to the Stefan-Boltzmann radiation law, the following relation exists:

$$R = 0.16TA\phi E \left[\frac{1}{0.01\Theta_1^4} - \frac{1}{0.01\Theta_2^4} \right]$$

The constant in the above expression has been variously assigned to values ranging from 0.136 to 0.190.³ It was originally given as 0.152, but late work⁴ by Bauer and Moulin places it at 0.160, and it has ordinarily been quoted at 0.160.

The coefficient of absorption of a surface is the ratio of the amount of radiant heat absorbed to the amount of heat incident on the surface. Lampblack absorbs practically all heat rays impinging on its surface and reflects none; its coefficient of absorption, then, is unity. The coefficient of emission is the ratio of the heat actually radiated to the heat an ideal black body would radiate, and it is the same in value as the coefficient of absorption. The net coefficient between two surfaces is very nearly the product of the coefficients of both surfaces, as the heat transmitted will be diminished both in emission and in absorption.

ϕ is the mean of the solid angles subtended by one surface with respect to each elementary area of the other surface. A unit solid angle is bounded by a hemisphere and this is the most usual technical case. Rules cannot be given for evaluating ϕ under all circumstances; but as this matter is seldom given but scant consideration, it will here be taken up more in detail.

¹ Wiener, *Ber.*, 1872.

² British thermal unit.

³ C. F ry, *Compt. rend.*, 1909.

⁴ E. Bauer and M. Moulin, *Journal Physique*, 1910.

VALUES OF E.

Lampblack.....	1.00	Sheet lead.....	0.18
Interior of furnaces.....	0.90-0.95	Polished steel.....	0.17
New cast iron.....	0.87	Polished sheet iron.....	0.12
Common steam pipe.....	0.85	Polished brass.....	0.07
Glass.....	0.80	Polished tin.....	0.06
Ordinary sheet iron.....	0.76	Polished copper.....	0.06
Polished zinc.....	0.19	Polished silver.....	0.03
Lampblack ¹	1.00	Mica.....	0.80
Paper.....	0.98	Graphite.....	0.75
Resin.....	0.96	Tarnished lead.....	0.45
Sealing wax.....	0.95	Mercury.....	0.20
Crown glass.....	0.90	Polished lead.....	0.19
India ink.....	0.88	Polished iron.....	0.12
Ice.....	0.85	Tin plate.....	0.12
Red lead.....	0.80	Gold, silver, copper.....	0.12
Lampblack ²	1.00	Building stone.....	0.90
Paper.....	0.94	Sawdust.....	0.88
Silk.....	0.92	Powdered charcoal.....	0.85
Wool.....	0.92	Powdered chalk.....	0.83
Oil paint.....	0.92	Glass.....	0.73
Calico.....	0.91	Zinc.....	0.56
Fine sand.....	0.90	Tin.....	0.05
Wood.....	0.90	Polished copper.....	0.04
Plaster.....	0.90	Polished silver.....	0.03

As far as radiation is concerned, a perfectly plane or even surface will radiate just as much heat as a rough, corrugated, or irregular surface of the same extent as far as boundaries are concerned. For a rough surface, the true value of ϕ would be less, and the true value of A greater than for a smooth surface of the same extent. With heat radiation, then, all surfaces may be treated as though they were smooth, an assumption which would be impermissible with heat conduction and convection.

In Fig. 1, the plane A_{11} subtends a mean solid angle of ϕ_1 hemispheres with respect to A_1 and it is desirable to express ϕ_1 in terms of quantities which may be more easily estimated than solid angles.

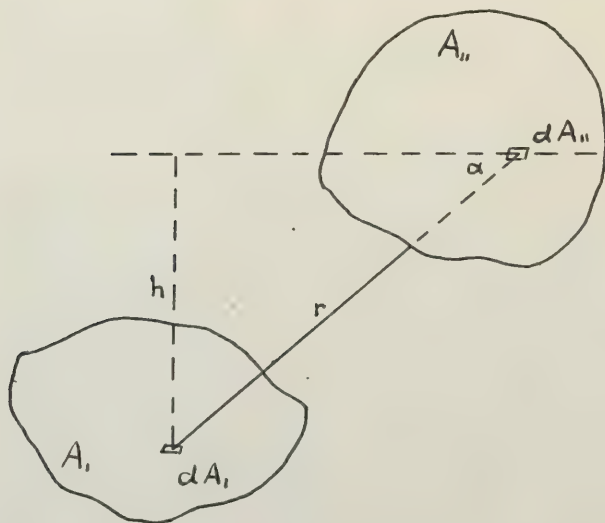


Fig. 1.

Both A_1 and A_{11} may be divided into elementary areas dA_1 and dA_{11} whose distances apart are r , and where the lines r connecting these make angles α with the surface of A_{11} at dA_{11} . Then, if ϕ is the solid angle subtended by dA_{11} with respect to dA_1 , its value is

$$\phi = \frac{dA_{11} \sin \alpha}{2\pi r^2}.$$

¹ Leslie, Watts' "Dictionary of Chemistry."

² Ser, *Physique industrielle*.

By definition, the mean solid angle ϕ_1 is

$$\phi_1 = \frac{\int \phi dA_1}{\int dA_1} = \frac{\iint \frac{dA_1 dA_{11} \sin \alpha}{2\pi r^2}}{A_1} = \frac{A_{11}}{2\pi} \left(\frac{\sin \alpha}{r^2} \right)_m.$$

Here $\left(\frac{\sin \alpha}{r^2} \right)_m$ is the mean of all values of $\frac{\sin \alpha}{r^2}$ between dA_1 and dA_{11} . For regular surfaces this could be obtained exactly by calculus, but in general practice, it will be close enough to obtain it by estimation, or by averaging a representative series of values of $\frac{\sin \alpha}{r^2}$ between evenly distributed points on the two surfaces.

When the surfaces are planes and parallel, then $\sin \alpha = \frac{h}{r}$ where h is the perpendicular distance between the planes. Then,

$$\phi_1 = \frac{h A_{11}}{2\pi} \cdot \frac{1}{r_m^3}.$$

r_m is the mean distance from any point in plane A_1 to any point in A_{11} and may generally be taken as the mean between the maximum and minimum distances between the surfaces. Also,

$$\phi_{11} = \frac{h A_1}{2\pi} \cdot \frac{1}{r_m^3};$$

hence,

$$\frac{\phi_1}{\phi_{11}} = \frac{A_{11}}{A_1}$$

or

$$A_1 \phi_1 = A_{11} \phi_{11}.$$

The fundamental law of heat conduction is expressed in the following relation, where Q is the heat units transmitted in T hours through a wall whose conductance is G units and under a temperature drop of Δ degrees:

$$\frac{Q}{T} = \Delta G$$

A similar though arbitrary relation will be assumed to hold for the heat units R radiated in T hours under a temperature drop Δ degrees from or to a surface whose radiant conductance is C ,

$$\frac{R}{T} = \Delta C.$$

H is the total heat transmitted where radiation and conduction occur simultaneously:

$$H = Q + R = \Delta T(C + G)$$

And just as the conductivity $g = \frac{G}{A}$ where A is the area of the wall or surface in square feet, so the radiant conductivity $c = \frac{C}{A}$.

In referring to actual experiments, it is convenient to refer to a value $K = \frac{H}{\Delta T} = C + G$, and to a value

$$k = \frac{K}{A} = c + g.$$

In the light of the Stefan-Boltzmann radiation law, it will be of advantage to investigate the significance of c ,

$$c = \frac{R}{\Delta T},$$

and

$$R = 0.16TA\varphi E \left[\frac{0.01\Theta_1}{0.01\Theta_1 - 0.01\Theta_{11}} \right]^4.$$

The ratio of Θ_{11} to Θ_1 will hereafter be referred to as a . Then,

$$R = 0.16TA\varphi E 0.01\Theta_1 (1 - a^4),$$

but

$$(1 - a^4) = (1 - a)(1 + a + a^2 + a^3)$$

and

$$0.01\Theta_1(1 - a) = 0.01\Theta_1 - 0.01\Theta_{11} = 0.01\Delta;$$

hence,

$$R = 0.0064TA\varphi E 0.01\Theta_1 \Delta \left[\frac{1}{4(1 + a + a^2 + a^3)} \right]$$

and

$$c = 0.0064\varphi E 0.01\Theta_1 \left[\frac{1}{4(1 + a + a^2 + a^3)} \right].$$

In the following plot (Fig. 2), $1 - a^4$, $1/4(1 + a + a^2 + a^3)$, and a as ordinates are plotted against a as abscissae. It can readily be seen that a does not vary greatly from $1/4(1 + a + a^2 + a^3)$ where $a > 0.3$. Since $a = \frac{0.01\Theta_{11}}{0.01\Theta_1}$ an approximate expression for c is

$$c = 0.0064\varphi E 0.01\Theta_1 \frac{1}{4(1 + a + a^2 + a^3)}.$$

The usual case of combined heat radiation and conduction is where heat passes from a surface at temperature ${}^{\circ}\theta_1$ through a space of approximately the same temperature, a conducting wall of thickness

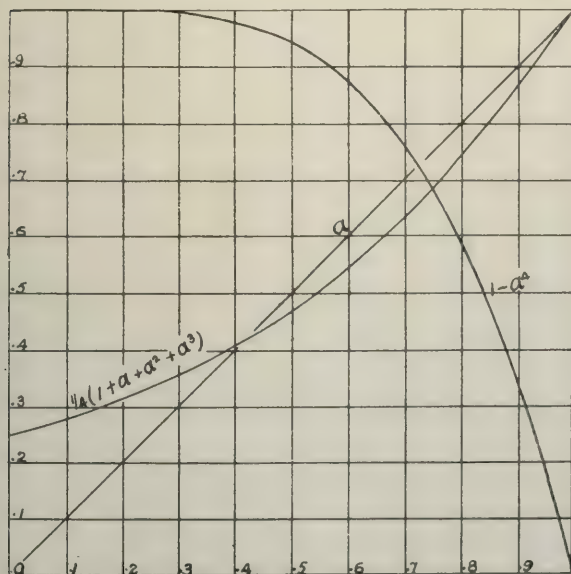


Fig. 2.

δ inches whose outside temperatures are ${}^{\circ}\theta_1$ and ${}^{\circ}\theta_{11}$, and into a fluid of temperature ${}^{\circ}\theta_{11}$. The internal resistivity of the wall is ρ . At ${}^{\circ}\theta_{11}$ the conductivity is γ_1 and the radiant conductivity is c_1 , and at ${}^{\circ}\theta_1$ the boundary resistivity is ζ_{11} . Both ${}^{\circ}\theta_1$, ${}^{\circ}\theta_{11}$, and $\Delta = {}^{\circ}\theta_1 - {}^{\circ}\theta_{11}$ are known, but ${}^{\circ}\theta_{11}$

and ${}^{\circ}\theta_1$ are not known. H heat units are transmitted in T hours (see Fig. 3).



Fig. 3.

Then,

$$\frac{H}{T} = \frac{\Delta A}{\frac{1}{\gamma_1 + c_1} + \delta\rho + \zeta_{11}}.$$

Very commonly, the quantities $\delta\rho$ and ζ_{11} may be neglected in comparison with $\frac{1}{\gamma_1 + c_1}$ and

$$\frac{H}{T} = \Delta A(\gamma_1 + c_1).$$

Since the temperature drops are proportional to the included resistivities, then,

$$\frac{{}^{\circ}\theta_1 - {}^{\circ}\theta_{11}}{\frac{1}{\gamma_1 + c_1}} = \frac{{}^{\circ}\theta_{11} - {}^{\circ}\theta_1}{\delta\rho} =$$

$$\frac{{}^{\circ}\theta_1 - {}^{\circ}\theta_{11}}{\zeta_{11}} = \frac{\Delta}{\frac{1}{\gamma_1 + c_1} + \delta\rho + \zeta_{11}}.$$

Generally $\delta\rho$ may be neglected especially for metallic walls, but if $\delta_1\rho_1$ representing the thickness of material like boiler scale multiplied into its internal resistivity, it cannot be neglected:

$${}^{\circ}\theta_1 - {}^{\circ}\theta_{11} = \zeta_{11}\Delta(\gamma_1 + c_1)$$

$${}^{\circ}\theta_{11} - {}^{\circ}\theta_1 = \delta_1\rho_1\Delta(\gamma_1 + c_1)$$

$$\frac{{}^{\circ}\theta_{11} - {}^{\circ}\theta_1}{\frac{1}{\gamma_1 + c_1} + \delta_1\rho_1} = \frac{\delta_1\rho_1\Delta}{1 + \delta_1\rho_1(\gamma_1 + c_1)} \Delta.$$

A few samples will demonstrate the practical application of these formulae. In a steam boiler the temperature of the steam is 250° [$=710^{\circ}$ absolute], the temperature of the grate is 1200° [$=1660^{\circ}$ absolute], and the thickness of the boiler plate is $1/4$ inch. It is now desired to find the temperature difference between the water side and the fire side of the plates exposed to direct radiation, where the value of $\rho = 0.003$, $\gamma_1 = 3$ and $\phi = 0.70$:

$$0.01\Theta_1 = 16.6 \quad 0.01\Theta_{11} \approx 7.1$$

$$-2$$

$$c_1 = 0.006 \times 0.70 \times 16.6 \times 7.1 = 8.2$$

$$c_1 + \gamma_1 = 11.2$$

$$t_{0,11} - t_{0,1} = 950 \times \frac{1}{4} \times 0.003 \times 11.2 = 8^\circ$$

If instead, copper plate had been used of $\frac{1}{2}$ inch thickness and 0.003 internal resistivity, then,

$$t_{0,11} - t_{0,1} = 950 \times \frac{1}{2} \times 0.003 \times 11.2 = 1.6^\circ.$$

It is here assumed that the copper plate has been sooted over, and E is around 0.95 instead of 0.05 were the copper polished.

These temperature drops of 1 per cent. and $\frac{1}{6}$ per cent. of the total temperature drop are absolutely negligible in comparison with the inaccuracy of data and assumptions. Blechynden¹ in experiments on the heat transmission of iron and copper plates exposed to combustion found no appreciable difference.

With boiler scale, it is quite different. Under the same conditions as before, it will be assumed that the heating surface is coated with a boiler scale of $\frac{1}{2}$ inch thickness and of internal resistivity 0.07, a fair value.

$$t_{0,11} - t_{0,1} = 950 \times \frac{\frac{1}{2} \times 0.07 \times 11.2}{1 + \frac{1}{2} \times 0.07 \times 11.2} = 270^\circ,$$

$$t_{0,11} = 520^\circ [= 980^\circ \text{ absolute}].$$

If the temperature of the boiler plate exposed to the fire of absolute temperature 1660° is 980° absolute instead of 710° , a new value for c should be solved, for

$$c = 0.006 \times 0.70 \times 16.6 \times 9.8 = 11.4$$

$$\gamma = 3 \quad \gamma + c = 14.4$$

$$t_{0,11} - t_{0,1} = 950 \times \frac{\frac{1}{2} \times 0.07 \times 14.4}{1 + \frac{1}{2} \times 0.07 \times 14.4} = 320^\circ,$$

$$t_{0,11} = 570^\circ.$$

As the decrease in heat transmission is proportional to the ratio of the resistance of the boiler scale to the total resistance, this means a decrease of 33 per cent. on the heat transmitted were no new scale present.

Under the same conditions the temperature drop $t_{0,11} - t_{0,1}$ from the water side of the plate to the mean temperature of the water may well be investigated. Here ζ_{11} ranges from 0.001 to 0.01, but in common practice with good circulation, ζ_{11} would not much exceed 0.002. This would mean a temperature drop of 20° in 950° of total temperature drop, that is, only 2 per cent. Had a sluggish liquid like sulphuric acid been evaporating in a platinum or cast iron still, the value of ζ_{11} would probably exceed 0.01 and 0.02 and would impose a large temperature drop on the boundary between the metal and the liquid.

The common problem of determining the loss of heat from steam pipe may readily be handled by this method of analysis. A steam pipe of 80 feet length and 3 inches diameter is covered with a 1-inch packing of asbestos. The temperature of the steam is 275° , and of the outside air and surroundings 80° [$= 540^\circ$ absolute]; and it is desired to find the hourly condensation of steam in the pipe. Other data to be given is $\rho_1 = 1.1$ for asbestos, $\zeta_{11} = 0.0004$ from steam to metal, a very low value, $\gamma = 0.45$ from the surface of the asbestos to air, $\phi = 1$, and $0.0064E = 0.005$:

¹ *Engineer*, 1896.

$$T = \frac{H}{\frac{\zeta_{11}}{A_{11}} + \frac{\delta_{11}\rho_1}{A} + \frac{1}{A_1(\gamma_1 + c_1)}}$$

$$A_{11} = \frac{80 \times 3 \times \pi}{12} = 63 \quad A = \frac{80 \times 4 \times \pi}{12} = 84$$

$$A_1 = \frac{80 \times 5 \times \pi}{12} = 105$$

$$-3$$

$$\delta_{11}\rho_1 = 1.1 \quad c_1 = 0.005 \times 5.4 = 0.8 \quad \gamma_1 + c_1 = 1.25 \quad \Delta = 195$$

The value of c_1 here is incorrect. On this assumption, the total resistance is 0.0206 while the outside surface resistance is 0.0076 which means a temperature drop of 72° , an outside surface temperature of

$$152^\circ \text{ which is } 613^\circ \text{ absolute. Hence } a = \frac{541}{613} = 0.88$$

$$\text{and } 1/4(1 + a + a^2 + a^3) = 0.84.$$

$$-3$$

$$c_1 = 0.005 \times 6.13 \times 0.84 = 0.97$$

$$T = \frac{H}{\frac{195}{0.000006 + 0.013 + 0.0067}} = 9900 \text{ B. t. u.}$$

= 10.8 pounds of steam condensed per hour.

A simple practical application of the combined conduction and radiation of heat is the investigation of the resistivities of air spaces of furnace walls at high and low temperature, and the resistivities of the same thicknesses of fire-brick.

In a furnace wall where the mean temperature is 1000° , an air space of 2 inches is left open to act as a non-conductor of heat. The value of $0.0064E$ will be assumed at 0.004 and the value of γ for either surface at 0.4, consequently the resultant conductivity of both surfaces in series with respect to the flow of heat is $1/2\gamma = 0.2$:

$$c = 0.004 \times 10 + 4.6 = 12.5$$

$$c + 1/2\gamma = 12.7$$

$$\frac{\Delta T}{H} = \frac{1}{12.7} = 0.08$$

Had the air space been filled in with fire brick with $\rho = 0.14$, then,

$$\frac{\Delta T}{Q} = \delta\rho = 2 \times 0.14 = 0.28.$$

This shows that it would be better to have the space filled in with fire brick, as it would offer greater resistance to the flow of heat. Had the space been

$$\frac{1}{4} \text{ inch in thickness, } \frac{\Delta T}{H} = 0.08 \text{ as before, but}$$

$\frac{\Delta T}{Q} = 0.04$, in which instance, the air space would offer the greater resistance. Had the mean temperature of the space been 100° instead of 1000° , then,

$$c = 0.004 \times 1 + 4.6 = 0.7$$

$$c + 1/2\gamma = 0.9$$

$$\frac{\Delta T}{H} = \frac{1}{0.9} = 1.1$$

and

$$\frac{\Delta T}{Q} = 0.28.$$

In this case the air space would offer more resistance. This has been well brought out both by experiment and by calculation by Ray and Kreisinger¹ in "The Flow of Heat through Furnace Walls." Hence a practical criterion for air spaces for insulating purposes is

$$\delta < \frac{1}{\rho(0.2 + c)}$$

The effectiveness of the heating surface of boilers may as readily be investigated by application of the laws of heat radiation and conduction as by the use of empirical formulae derived from experiment, since in the latter, factors are often omitted that are taken into account by the former. The amount of heat absorbed from hot gases in fire tubes is a problem involving the laws of heat conduction and convection alone, the solution of which has been previously outlined. The problem of determining the heat absorbed directly from the furnace grate of a boiler depends on the assumption of the absolute temperature of the surface of the fuel. This depends on the heating value of the fuel, the rate of fuel and air supply, and to a certain extent, on the velocity of reactions involved. It is probably simpler to assume an absolute grate temperature and work backward to determine what combinations of these factors will satisfy this assumption than it is to determine the temperature of combustion from these factors, but that lies outside the scope of this paper.

The calculation of the heat-transmitting capacity of the heating surface of the combustion chamber of internally fired boilers presents no difficulties. All areas are known. The temperature of the heating surface is the same approximately as the temperature of the steam. The grate is at an assumed or known absolute temperature and it radiates heat in all directions to a surface of known temperature. The heat absorbed by conduction may be calculated from the assumed or calculated velocity of the gases of combustion.

In the case of an externally fired boiler, the conditions are not so simple. The area A_1 of the grate surface, the area A_{11} of the boiler-heating surface opposite, and the area A of the furnace walls included between these are all known. The value of ϕ , the mean solid angle subtended by A_{11} with respect to A_1 , may be determined by estimating r_m the mean distance between the surfaces. The temperature θ_1 of the surface of the fuel is assumed, and the temperature of the boiler surface θ_{11} is known, but the temperature of the furnace walls θ is not known. Now it is clear that heat passes from the fuel bed to the boiler surface in four different ways: (1) heat is radiated from the grate at an absolute temperature θ_1 to the boiler surface at an absolute temperature θ_{11} ; (2) heat is conducted from the hot products of combustion at a temperature somewhat less than θ , to the boiler surface at θ_{11} by conduction; (3) heat is radiated from the fuel surface to the furnace walls at an unknown temperature $\theta - \theta_1$ and θ_{11} and from thence radiated to the boiler surface A_{11} ; and (4) heat is con-

ducted into the furnace walls, so the effect of (4) on θ may be neglected. The first step is to determine the mean absolute temperature Θ of the furnace walls. The heat radiated from the fuel surface to the furnace walls equals the heat radiated from these to the boiler. It will be assumed that $0.16E = 0.14$.

$$0.14A_1(1 - \phi_1)[0.01\theta_1 - 0.01\Theta] = 0.14A_{11}(1 - \phi_{11})[0.01\Theta - 0.01\theta_{11}]$$

$$\frac{A_1(1 - \phi_1)}{A_{11}(1 - \phi_{11})} = \frac{1 - \phi_1}{1 - \phi_{11}} = N = \frac{0.01\Theta - 0.01\theta_{11}}{0.01\theta_1 - 0.01\Theta}$$

Since ϕ , A_1 , and A_{11} are known, the value N is known and it commonly varies from 1 to 0.5.

$$0.01\Theta = \frac{4}{N + 1} \sqrt{N \cdot 0.01\theta_1 + 0.01\theta_{11}}$$

If $a = \theta_{11}/\theta_1$ and $a_1 = \Theta/\theta_1$, R can now be solved, for

$$R = 0.14A_1 T_{0.01\theta_1} [\phi_1(1 - a^4) + (1 - \phi_1)(1 - a_1^4)]$$

With respect to A_{11} , the value c may be obtained by dividing R by $A_{11}\Delta T$, where $\Delta = \theta_1 - \theta_{11}$.

$$c = 0.14 \frac{A_1}{A_{11}} \frac{0.01\theta_1}{\Delta} [\phi_1(1 - a^4) + (1 - \phi_1)(1 - a_1^4)]$$

and

$$k = c + g = \frac{H}{\Delta T}$$

A common formula for g in terms of the pounds of coal B burned per square foot of grate surface per hour is

$$g = 0.4 + 0.9\sqrt{B}$$

The classical researches of Blechynden are often quoted to show that heat transfer from hot furnace gases is proportional to the square of the temperature drop. Formulas of Rankin, Werner, and others assume that heat transfer at high temperatures is proportional to the square of the temperature difference.

It would not be out of place to present here some experimental data obtained by Blechynden³ on this point. The furnace was cylindrical in shape of 12 1/2 inches internal diameter, above which was supported a cylindrical vessel of 10 inches diameter and 12 inches height. The furnace was heated by five jets of illuminating gas mixed with air, and these played upon a layer of asbestos so as to provide an even heat. The vessel rested upon a conical mantle provided with four exit pipes to carry away the products of combustion, of which the temperature was taken by means of a pyrometer, as was also the temperature just above the asbestos grate. The three moduli obtained by Blechynden may be expressed in terms of the

¹ Bull. 8, Bureau of Mines

² $A_1\phi_1 = A_{11}\phi_{11}$

³ Proc Inst. Nav. Arch., 1894; Engineer, 1893

temperature θ_1 of the asbestos grate, θ of the heating gases, and $\theta_{11} = 212$, the temperature of the vessel. H, A and T have the usual significance.

$$\mu = \frac{H}{AT(\theta - \theta_{11})} \quad \mu' = \frac{H}{AT(\theta - \theta_{11})(\theta_1 - \theta_{11})} \quad \mu'' = \frac{H}{AT(\theta_1 - \theta_{11})}$$

Hence,

$$\mu'' = \mu' \left(\frac{\mu'}{\mu} \right).$$

Plate.	Thickness.	μ	μ'	$\frac{\mu'}{\mu}$	μ''
A.....	1 1/4"	0.0155
A.....	3/4"	0.0176
A.....	9/16"	0.0212
A.....	1/4"	0.0230
A.....	1/8"	0.0239
B.....	15/32"	0.0239
B.....	3/8"	0.0245
B.....	1/4"	0.0257
B.....	3/32"	0.0261	0.0206	0.79	0.0163
C.....	13/16"	0.0182
D.....	1/2"	0.0237	0.0174	0.74	0.0129
E.....	1 1/4"	0.0142	0.0097	0.68	0.0066
E.....	3/16"	0.0191	0.0142	0.74	0.0105
Average.....		0.0213	0.0155	0.74	0.0115

Another set of experiments were carried out at the Physikalisch-Technischen Reichsanstalt in 1895-96 in the same kind of apparatus. The temperatures θ were taken with a pyrometer at 1 1/2 inches below the center of the heating surface.

θ .	$\theta - \theta_{11}$.	$\frac{H}{AT}$.	$\frac{H}{AT(\theta - \theta_{11})}$.	$\mu' = \frac{H}{AT(\theta - \theta_{11})^2}$.
Plate thickness = 13/16".				
705	493	4400	8.92	0.0181
812	600	6050	10.08	0.0168
875	663	7610	11.47	0.0173
896	684	7970	11.65	0.0168
912	700	8820	12.60	0.0180
1042	830	11020	13.28	0.0160
1162	950	13760	13.96	0.0147
1209	997	15200	15.25	0.0153
1245	1033	17410	16.85	0.0163
Average,				0.0166
Plate thickness = 13/32".				
655	443	3200	7.23	0.0163
763	551	4800	8.71	0.0158
903	691	7500	10.85	0.0157
1117	905	12200	13.48	0.0149
Average,				0.0153
Plate thickness = 5/16".				
586	374	2370	6.32	0.0169
768	556	4980	8.95	0.0161
931	725	8730	12.04	0.0166
962	750	8280	11.03	0.0147
1064	852	11900	13.97	0.0164
Average,				0.0161
Plate thickness = 3/16".				
607	395	2540	6.44	0.0163
784	572	4775	8.35	0.0146
930	718	7720	10.77	0.0150
1122	910	13730	15.10	0.0166
Average,				0.0156

Since the temperature θ employed in these latter experiments is probably intermediate between the temperature of the asbestos grate and the temperature of the outgoing products of combustion, the mean value μ' here obtained is 0.0159, checks very close to μ' obtained by Blechynden 0.0155. If 0.0159 is multi-

plied by the mean value of $\frac{\mu'}{\mu}$, 0.0118 is obtained where Blechynden obtained 0.0115.

It is very clear from these experiments that the heat transmitted at high temperatures varies nearly as the square of the temperature difference. That this is in accord with the laws of heat radiation and conduction can be shown by applying the formulas on page 811 to a special case of heat transfer into an externally fired boiler from the combustion chamber

where $\frac{A_{11}}{A_1} = 1.2$, $\phi_1 = 0.6$ and consequently $N = 0.67$.

The temperature of the steam is 300° and the temperature at the grate varies from 1400° to 1000°. The value of $g = 2$.

θ_1 .	0.01 θ_1 .	0.01 θ_{11} .	Δ .	0.01 θ .	α .	α_1 .	c .	k .	$\mu'' = \frac{k}{\Delta}$.
1400	18.6	7.6	1100	14.95	0.41	0.80	10.4	12.4	0.0113
1300	17.6	7.6	1000	14.20	0.43	0.81	9.0	11.0	0.0110
1200	16.6	7.6	900	13.40	0.46	0.81	7.8	9.8	0.0109
1100	15.6	7.6	800	12.65	0.49	0.81	6.8	8.8	0.0110
1000	14.6	7.6	700	11.95	0.52	0.82	5.9	7.9	0.0113
Average,									0.0111

The value of $\mu'' = 0.0111$ checks very closely to the value 0.0115 obtained by Blechynden, and 0.0118 from the experiments later conducted. This is purely accidental. What is of importance is that results obtained by experimental investigation can be rationally duplicated by systematic application of the laws of heat radiation and conduction.

THE EFFECT OF ADDED FATTY AND OTHER OILS UPON THE CARBONIZATION OF MINERAL LUBRICATING OILS.¹

By C. E. WATERS.

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In a paper on "The Behavior of High-Boiling Mineral Oils when Heated in the Air,"² the author called attention to the fact that two straight mineral oils under investigation yielded more "carbonized" matter, insoluble in petroleum ether, when they were heated in brass tubes than when they were heated in glass tubes of the same dimensions. The reverse was true of a third oil having a saponification number indicating the presence of about 0.5 per cent. of fatty oil. This naturally suggested the advisability of determining the amount of carbonization of a straight mineral oil and of the same oil with known amounts of other constituents, such as lard oil, rosin oil, tallow, etc., added. The results of a series of such determinations are given in the present paper.

The oil selected was an engine oil flashing at 140° in the Pensky-Martens closed cup apparatus. For the first tests there were seven samples as follows:

No. 1. The straight mineral oil. When 10 grams, diluted with 50 cc. of petroleum ether, were allowed to stand over night, it yielded only traces of precipitate. These proportions of oil and solvent are the same as adopted in the carbonization tests.

No. 2. The mineral oil heated with "ivory" soap.

¹ Published by permission of the Director of the Bureau of Standards.

² Bull. Bur. Standards, 7, 365 (1911); THIS JOURNAL, 3, 233 (1911).

shavings for several hours in a closed flask on the steam-bath. It was allowed to stand over night and then filtered. After standing several weeks in a closed bottle it set to a sort of jelly, but became perfectly fluid on shaking and remained so. Very little soap was in solution, for it gave only 0.03 per cent. of ash.

No. 3. The mineral oil saturated with rosin in the same way as with soap. It yielded only 0.03 per cent. of insoluble in petroleum ether.

No. 4. A 10 per cent. solution of rosin oil in mineral oil.

No. 5. A 10 per cent. solution of rapeseed oil in mineral oil.

No. 6. A 10 per cent. solution of lard oil in mineral oil.

No. 7. A 5 per cent. solution of tallow in mineral oil. It yielded 0.20 per cent. of insoluble in petroleum ether.

As shown in the earlier paper, and confirmed by other determinations to be mentioned later, the insoluble precipitate is an oxidation product. It ought, therefore, to vary in amount with the time of heating and with the surface of oil exposed to the air. Hence the first thing necessary was to obtain a set of flasks as nearly alike as possible in internal diameter and in bore of neck. Erlenmeyer flasks of Jena glass were used, and by measuring all that were on hand with a pair of inside calipers made for the purpose, a sufficient number of almost exactly the same dimensions was obtained. Their inside diameter at the widest part was 65 mm., and the bore of the neck 21 mm. They were of 150 cc. capacity.

For each determination approximately 10-gram samples were weighed into the flasks, which were then heated to 250° for 5 hours (instead of 3 hours as in the earlier work) in the air-bath described in the former paper. The flasks, it may be remembered, were suspended by their necks from openings cut in the cover of the bath, and there was perfect freedom of diffusion of oil vapors and air. After cooling, the flasks were wiped off and weighed to determine the loss by volatilization. Then after adding 50 cc. of petroleum ether, corking and shaking the flasks with a gentle rotary motion until the thick residue went into solution as completely as possible, the flasks were allowed to stand about 22 hours. This length of time seemed to be necessary for complete precipitation and agglomeration of the insoluble matter in a form admitting of easy filtration. If it stood only about 16 hours it was far less manageable.

The insoluble matter was filtered off on a Gooch crucible prepared with a disk of blue ribbon paper (cut with a cork borer), covered with a fairly thick felt of fine asbestos. The residue on the filter was washed with petroleum ether and dried at 93-95° before weighing. Attempts to dry at the traditional 105°, in some of our earlier work, showed that there was danger of melting the precipitate. The flasks were, of course, thoroughly rinsed with petroleum ether to remove all oil and precipitate. They were also heated to the same temperature and weighed

in order to determine the amount of varnish-like coating on the walls.

During the dry cold weather when a large part of the work was done, it was found difficult to entirely avoid static electrical disturbances when weighing. But the errors so caused could not have amounted to more than 2 mg., a negligible quantity in weighing the flasks. The precaution was always taken to touch the balance pan with the finger two or three times in making the final adjustment of the rider.

In making the determinations, four flasks, usually with a different sample in each, were heated at one time. The set of twelve flasks was also used in regular rotation as far as possible. These precautions were taken in order to eliminate accidental variations caused by irregular heating, differences in the dimensions of the flasks, and possible catalytic effects due to the walls of the flasks, as suggested in the first paper.

It may appear to be unnecessary, but for the sake of completeness the flask numbers and the number of each heat are included among the data.

NO. 1.—STRAIGHT MINERAL OIL.

Flask No.....	1	8	3	10	5	12	3	6	
Heat No.....	1	2	4	6	8 ¹	9	11	13	Avs.
Evaporation,									
per cent.....	61.5	47.8	38.8	34.0	34.9	39.5	45.1	51.0	...
"Varnish," per									
cent.....	0.46	0.35	0.39	0.30	0.12	0.60	0.25	0.20	0.33
Insoluble, per									
cent.....	2.60	2.46	2.07	2.02	1.74	2.65	2.20	2.33	2.26
Total residue,									
per cent.....	3.06	2.81	2.46	2.32	1.86	3.25	2.45	2.53	2.59

NO. 2.—MINERAL OIL CONTAINING SOAP.

Flask No.....	2	9	4	11	6	5	4	7	
Heat No.....	1	3	4	6	8 ¹	10	11	13	Avs.
Evaporation,									
per cent.....	37.1	45.0	43.8	50.9	45.9	42.1	52.9	48.8	...
"Varnish," per									
cent.....	0.13	0.13	0.14	0.04	0.12	0.05	0.14	0.10	0.11
Insoluble, per									
cent.....	1.96	2.08	1.93	1.92	1.89	1.78	2.61	2.27	2.06
Total residue,									
per cent.....	2.09	2.21	2.07	1.96	2.01	1.83	2.75	2.37	2.17

NO. 3.—MINERAL OIL CONTAINING ROSIN.

Flask No.....	5	12	7	2	9	8	11	2	
Heat No.....	1	3	5	6	8 ¹	10	12	13	Avs.
Evaporation,									
per cent.....	47.1	49.2	40.0	35.1	32.9	51.0	60.2	38.4	...
"Varnish," per									
cent.....	0.16	0.19	0.27	0.20	0.46	0.35	...	0.28	0.27
Insoluble, per									
cent.....	2.22	2.18	1.96	1.83	2.34	2.72	2.51	2.25	2.25
Total residue,									
per cent.....	2.38	2.37	2.23	2.03	2.80	3.07	...	2.53	2.52

NO. 4.—MINERAL OIL CONTAINING ROSIN OIL.

Flask No.....	4	11	6	1	8	7	10	1	
Heat No.....	1	3	5	7	8 ¹	10	12	14	Avs.
Evaporation,									
per cent.....	44.1	47.2	56.1	65.5	41.7	36.7	34.4	53.5	...
"Varnish," per									
cent.....	0.34	0.16	0.14	0.40	0.20	0.18	...	0.07	0.21
Insoluble, per									
cent.....	1.84	2.02	2.10	2.59	1.79	1.90	1.76	1.19	1.90
Total residue,									
per cent.....	2.18	2.18	2.24	2.99	1.99	2.08	...	1.26	2.11

¹ In heat No. 8 there was some difficulty in regulating the temperature

No. 5.—MINERAL OIL CONTAINING RAPESEED OIL.

Flask No.....	5	12	2	9	8	11	2		
Heat No.....	2	3	5	7	9	10	12	14	Avs.
Evaporation, per cent.....	36.4	50.1	48.6	44.6	34.4	43.2	45.1	26.8	..
"Varnish," per cent.....	1.39	1.35	1.45	1.36	1.55	1.85	..	0.67	1.37
Insoluble, per cent.....	0.01	0.01	0.02	0.01	0.02	0.01	0.01	0.02	0.01
Total residue, per cent.....	1.40	1.36	1.47	1.37	1.57	1.86	..	0.69	1.38

The reason for the apparently low percentage of "insoluble" and the high percentage of "varnish" is that the flocculent precipitate at first thrown out of the heated oil by the petroleum ether collected, on standing, in small, hard lumps on the bottom of the flask and could not be washed out. No. 6, containing lard oil, showed a tendency in the same direction, but the residue was easily dislodged by a strong stream of petroleum ether from a wash-bottle.

No. 6.—MINERAL OIL CONTAINING LARD OIL.

Flask No.....	6	1	8	3	10	1	12	3	
Heat No.....	2	4	5	7	9	11	12	14	Avs.
Evaporation, per cent.....	42.0	51.6	52.2	49.2	43.6	49.0	45.2	33.9	..
"Varnish," per cent.....	0.08	0.03	0.04	0.06	0.24	0.02	..	0.18	0.09
Insoluble, per cent.....	0.31	0.31	0.33	0.61	0.46	0.32	0.55	0.28	0.40
Total residue, per cent.....	0.39	0.34	0.37	0.67	0.70	0.34	..	0.46	0.49

No. 7.—MINERAL OIL CONTAINING TALLOW.

Flask No.....	7	2	9	4	11	2	5	4	
Heat No.....	2	4	6	7	9	11	13	14	Avs.
Evaporation, per cent.....	45.5	38.1	47.9	46.6	41.9	46.8	40.2	35.6	..
"Varnish," per cent.....	0.10	0.06	0.07	0.05	0.12	0.13	0.09	0.29	0.11
Insoluble, per cent.....	1.35	1.27	1.38	1.47	1.43	1.49	1.25	1.31	1.37
Total residue, per cent.....	1.45	1.33	1.45	1.52	1.55	1.62	1.34	1.60	1.48

The percentages of "insoluble" here given are not corrected for the amount (0.20 per cent.) thrown out by petroleum ether before the oil was heated.

A second sample of engine oil, purporting to be the same as No. 1, was obtained, since no more of the latter was available, and it seemed advisable to make some determinations on several mixtures not thought of at first. The descriptions of these new mixtures follow:

No. 8. New sample of mineral oil.

No. 9. Mineral oil, to every 10 grams of which was added 0.25 gram of Syrian asphalt dissolved in 25 cc. of xylene. The solution was always added after the oil was weighed, and the solvent driven off by heating of the steam-bath, at the same time blowing a gentle current of air into the flask. Before heating to 250°, petroleum ether threw out 1.35 per cent. of insoluble.

No. 10. Mineral oil, to every 10 grams of which 0.01 gram of sulphur dissolved in 1 cc. of xylene was added. In this case the solvent was not driven off before heating.

No. 11. A 10 per cent. solution of 55° paraffin in mineral oil. This could be poured about as well as a heavy cylinder oil.

No. 12. A 10 per cent. solution of linseed oil in mineral oil.

No. 13. Mineral oil and soap. To every 10 grams of the oil there was added before heating 0.50 gram of finely powdered "ivory" soap, dried at 100–105°.

No. 14. Mineral oil oxidized by the combined action of air and sunlight, as described in an earlier paper.* The oil was placed in a crystallizing dish, in a layer about 1.5 cm. deep, covered with a second dish and exposed outside a southern window from February 21st until March 23rd. Every day or two the oil was thoroughly stirred.

No. 15. A mixture of the mineral oil with "Kahlbaum" ferric oxide. In each 10 grams of the mixture there was 0.086 gram of the oxide.

No. 16. Mineral oil oxidized in flasks, but otherwise like No. 14. The oxidation was carried out in this way in order to determine the gain in weight. The average for four flasks, all of which gained nearly the same amount, was 0.92 per cent. This figure represents absorbed oxygen minus carbon dioxide and a little water. The contents of the four flasks were mixed before determining the carbonization. Nearly all of the insoluble oxidation product remained on the walls of the flasks.

The results obtained on heating these oils under the same conditions as for oil 1 to 8 are here given.

No. 8.—SECOND SAMPLE OF MINERAL OIL.

Flask No.....	5	9	7	1new	11	1		
Heat No.....	1	2	4	8	9	12	Avs.	
Evaporation, per cent.....	41.1	34.6	43.6	60.1	49.1	44.0	..	
"Varnish," per cent.....	0.22	0.66	0.16	0.49	0.31	0.37	0.35	
Insoluble, per cent.....	2.08	2.73	1.98	3.18	2.50	2.58	2.51	
Total residue, per cent.....	2.30	3.39	2.14	3.67	2.81	2.95	2.86	

No. 9.—MINERAL OIL CONTAINING ASPHALT.

Flask No.....	6	5	8	9	5	2		
Heat No.....	1	4	4	9	10	12	Avs.	
Evaporation, per cent.....	46.1	31.0	35.3	37.9	30.6	34.4	..	
"Varnish," per cent.....	0.31	0.29	0.21	0.22	0.35	0.36	0.29	
Insoluble, per cent.....	4.95	4.55	4.40	4.55	4.66	4.84	4.66	
Total residue, per cent.....	5.26	4.84	4.61	4.77	5.01	5.20	4.95	

The percentages of insoluble here given are not corrected for the amount thrown out of the oil when petroleum ether is added before heating. As mentioned above, this was 1.35 per cent. The percentages given are figured on the basis of 10 grams of oil.

No. 10.—MINERAL OIL CONTAINING SULPHUR.

Flask No.....	7	6	12	10	6	3		
Heat No.....	1	4	5	9	10	12	Avs.	
Evaporation, per cent.....	36.4	65.2	36.0	33.4	37.0	34.7	..	
"Varnish," per cent.....	0.37	0.54	0.56	0.27	0.19	0.29	0.37	
Insoluble, per cent.....	2.81	3.34	2.57	1.89	2.14	2.39	2.52	
Total residue, per cent.....	3.18	3.88	3.13	2.16	2.33	2.68	2.89	

No. 11.—MINERAL OIL CONTAINING PARAFFIN.

Flask No.....	8	4	5	7	1			
Heat No.....	1	3	7	10	11	Avs.		
Evaporation, per cent.....	39.9	42.0	40.8	39.0	39.0	..		
"Varnish," per cent.....	0.37	0.15	0.15	0.40	0.41	0.30		
Insoluble, per cent.....	2.59	2.39	2.33	2.95	3.23	2.70		
Total residue, per cent.....	2.96	2.54	2.48	3.35	3.63	3.00		

No. 12.—MINERAL OIL CONTAINING LINSEED OIL.

Flask No.....	1	2	6	8	2			
Heat No.....	3	3	7	10	11	Avs.		
Evaporation, per cent.....	50.5	33.0	48.6	36.0	48.1	..		
"Varnish," per cent.....	6.10	5.29	6.31	6.72	7.09	6.30		
Insoluble, per cent.....	0.02	0.03	0.01	0.01	0.01	0.02		
Total residue, per cent.....	6.12	5.32	6.32	6.73	7.10	6.32		

* Bull. Bur. Standards, 7, 227 (1911); This Journal, 2, 451 (1910)

The petroleum ether threw out a thick, tarry deposit that adhered to the bottom of the flask. This was necessarily counted in with the true "varnish."

NO. 13.—MINERAL OIL CONTAINING SOAP.

The contents of the flasks formed, after heating, a nearly solid cake, which could be broken up only with difficulty with petroleum ether. The residue was so fine-grained and gummy that it could not be filtered off.

NO. 14.—MINERAL OIL OXIDIZED IN CRYSTALLIZING DISHES

Flask No.	9	10	7	4	3	
Heat No.	5	5	7	8	11	Avs.
Evaporation, per cent.	47.7	44.6	42.1	51.6	44.9	
"Varnish," per cent.	0.34	0.30	0.31	0.16	0.26	0.28
Insoluble, per cent.	5.69	6.06	5.64	5.87	6.76	6.00
Total residue, per cent.	6.03	6.36	5.95	6.03	7.03	6.28

NO. 15.—MINERAL OIL CONTAINING FERRIC OXIDE.

Flask No.	3	11	2	3	4	
Heat No.	3	5	8	8	11	Avs.
Evaporation, per cent.	35.5	51.5	57.1	42.4	44.3	
"Varnish," per cent.	1.11	0.57	1.59	0.60	1.23	1.02
Insoluble, per cent. (corr. for Fe ₂ O ₃)	7.30	4.91	6.58	5.05	8.66	6.50
Total residue, per cent.	8.41	5.49	8.17	5.65	9.89	7.52

The insoluble was corrected for ferric oxide by washing out the Gooch crucible with benzene. With one exception, the weight of the residue was about 2 mg., or 0.02 per cent., greater than the amount of ferric oxide known to be in 10 grams of the unheated oil-ferric oxide mixture. Hence the percentages of insoluble given above are somewhat too low. The exact amount of the discrepancy must be greater than 0.02 per cent., however, for a small part of the oxide remained in the ring of "varnish" adhering to the walls of the flasks. There were, besides, traces that could not be removed from the bottoms of the flasks even with the most careful washing with petroleum ether.

NO. 16.—MINERAL OIL OXIDIZED IN FLASKS.

Flask No.	8	12	4	
Heat No.	7	9	12	Avs.
Evaporation, per cent.	42.9	40.8	56.0	
"Varnish," per cent.	0.44	0.18	0.31	0.31
Insoluble, per cent.	7.30	6.12	7.65	7.02
Total residue, per cent.	7.74	6.30	7.96	7.33

In order to determine whether or not any "varnish" or insoluble is formed in the absence of air, 10-gram samples of each of the oils numbered 5, 6, 7 and 8 were heated in flasks with the mouths covered with ground glass plates. They were heated to 250° for 5 hours. In no case was there any "varnish" formed on the walls, and only traces of insoluble were thrown out by petroleum ether. The "loss by evaporation" represents largely the oil which condensed on the glass plates and dripped off or was wiped off the necks of the flasks before they were weighed.

Sample.	5	6	7	8
Evaporation, per cent.	3.56	5.42	4.64	5.30

DISCUSSION OF RESULTS.

In considering the percentages of insoluble obtained on heating any given sample of oil, it is evident that there are causes of variation that may or may not be capable of elimination. A frequent source of annoyance was the sudden changes in the temperature

of the air-bath. In all of this work two thermometers, which gave almost identical readings when heated side by side in an oil-bath, were used on opposite sides of the air-bath with their bulbs on a level with the oil in the flasks. They were only 8 cm. apart, yet would often differ 10° in their readings. Frequently they would be not more than a degree apart for an hour or more, and then one or both would show a change in temperature; or first one and then the other would show a higher reading. The copper bath, with a double bottom and sheathed on the sides with a double layer of asbestos with a 3 mm. air-space between, was heated by a burner with a "rose" top giving a uniformly spreading flame. The flasks were only about one centimeter apart at their widest part and the thermometer bulbs were between opposite pairs of flasks. It seemed, therefore, as if the reactions of cracking and oxidation, which are endothermic and exothermic respectively, might have something to do with the sudden variations.

It is also possible that air currents might have caused more or less of the products of combustion from the burner, and hence varying amounts of oxygen, to encircle the necks of the flasks on one side of the bath and thus lower or raise the amounts of insoluble formed. It is hoped to eliminate this possible source of variation and also the irregular heating by means of an electrically heated bath now being made.

The results given in the present paper show, as did those published before, that there is no apparent connection between the amounts of insoluble, evaporation and "varnish."

As to catalytic action, influencing the amount of insoluble, which was hinted at in the earlier paper, a tabulation of the present results fails to give any certain evidence of it.

In the following table are brought together the average values for "varnish," insoluble and total residue for each of the mixtures. There are also given the averages calculated after striking out the most widely variant values, with the exception of those for No. 15, all of which differed so much among themselves that a recalculation would mean nothing.

TABLE SHOWING AVERAGE RESULTS.

		All values included.			Aberrant values omitted.		
Sam- ple.	Contains:	"Var- nish."	Insol- uble.	Total residue.	"Var- nish."	Insol- uble.	Total residue.
1.	Min. oil.....	0.33	2.26	2.59	0.32	2.21	2.53
2.	Soap.....	0.11	2.06	2.17	0.13	1.93	2.06
3.	Rosin.....	0.27	2.25	2.52	0.24	2.30	2.54
4.	Rosin oil.....	0.21	1.90	2.11	0.17	1.90	2.07
5.	Rapeseed oil...	1.37	0.01	1.38	1.42	0.01	1.43
6.	Lard oil.....	0.09	0.40	0.49	0.05	0.31	0.36
7.	Tallow.....	0.11	1.37	1.48	0.09	1.37	1.46
8.	Min. oil (2)...	0.35	2.51	2.86	0.35	2.60	2.95
9.	Asphalt.....	0.29	4.66	4.95	0.29	4.66	4.95
10.	Sulphur.....	0.37	2.52	2.89	0.31	2.59	2.90
11.	Paraffin.....	0.30	2.70	3.00	0.39	2.44	2.83
12.	Linseed oil...	6.30	0.02	6.32	6.38	0.02	6.40
14.	Oxidized min. oil.....	0.28	6.00	6.28	0.30	5.82	6.12
15.	Fe ₂ O ₃	1.02	6.50	7.52			
16.	Oxidized min. oil.....	0.31	7.02	7.33	0.31	7.32	7.63

Comparing the results of Nos. 1 to 7, it is evident that, with the exception of adding rosin, the admixture

of other oils to the mineral oil has caused a greater or less diminution in the amount of insoluble and of total residue. The same is also true of the "varnish," for, as already explained, the apparently high values obtained for No. 5 were caused by the adherence of the insoluble precipitate to the bottom of the flask.

Considering Nos. 8 to 16, we see that the addition of asphalt increases the percentage of insoluble. This is true even if we correct the figures given in the table by the amount precipitated by petroleum ether before the mixture is heated. This is equivalent to 1.35 per cent. calculated on the basis of 10 grams of oil.

The addition of sulphur, contrary to expectation, caused no marked difference. The same is true of the addition of paraffin. Linseed oil, as was to be expected, enormously increased the amount of total residue.

The oil which was exposed to the action of sunlight and air in flasks was, presumably, more completely oxidized than that in the crystallizing dish, for it was in a thinner layer and, besides, the flasks were rotated each day so as to spread the oil on the walls. It is not surprising that the figures obtained on heating this oil are higher than those for No. 14.

The results obtained with the mixture containing ferric oxide are interesting, especially in connection with the statement of Worrall and Southcombe,¹ that the horny or granular deposit at times found in steam cylinders is Fe_2O_3 or Fe_3O_4 cemented together by oil. One would not expect to find much rusting in the cylinder or carbureter of a gas engine, but it is not impossible that the fine metallic powder resulting from the wearing of the piston and of the cylinder walls may become oxidized and then further the carbonization of the lubricant.

CONCLUSIONS.

It has been shown that the addition of various oils and other substances to a straight mineral oil affects the amount of carbonization, as measured by the percentage of precipitate thrown out by petroleum ether, in various ways. Lubricants containing soap in quantity (see No. 13), rosin and asphalt, or which have been exposed to the action of sunlight and air, are to be avoided.

One must not conclude, however, from the low results obtained with mixtures containing tallow, lard oil, etc., that the addition of these oils is to be recommended. The presence of the fatty acids resulting from the decomposition of the oils may greatly increase the corrosion of the cylinder and in actual practice cause as much carbonization as the addition of ferric oxide would do.

It is intended in the near future to make a series of determinations by heating the above mixtures, and possibly others, with polished strips of iron, brass and other metals.

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¹ *J. Soc. Chem. Ind.*, **19**, 525 (1900).

THE FLUORESCENT TEST FOR MINERAL AND ROSIN OILS.

By PERCY H. WALKER AND E. W. BOUGHTON.

Received Sept. 23, 1911.

The Outerbridge method¹ of detecting and estimating mineral and rosin oils in fatty oils, by taking advantage of the fact that the fluorescence, which is a property of some oils, is very much magnified by examining the oil in the light of an inclosed arc, introduces an entirely new method of oil-testing. The author of this method has made the interesting discovery that samples of oil which in sunlight show no fluorescence, when examined by the light of an inclosed arc frequently show a very strong fluorescence. He further states that the examination of a large number of vegetable oils failed to show a trace of fluorescence in any of them, while all samples of heavy mineral and rosin oil, whether debloomed or not, showed strong fluorescence in the proper light. Based upon this observation, he proposes to rapidly detect and determine mineral or rosin oil in fatty oils by matching the fluorescence of the oil under examination with that of a prepared set of standard mixtures.

Outerbridge's statement that fluorescence is very greatly magnified by making the observation in the light of an inclosed arc has been verified in this laboratory. In addition to the lights used by Outerbridge, the uviolet light was tried but found to be in no way equal to the inclosed arc, which is far superior for this purpose to any other source of light.

Fluorescence in an oil does not, however, prove the presence of mineral or rosin oil. Of the 16 samples of pure linseed oil furnished by Committee D-1 of the American Society for Testing Materials, Nos. 3, 5, 6, 10, 12, 13, 14 and 16 showed no fluorescence, Nos. 1, 2 and 11 showed slight fluorescence and Nos. 4, 7, 8, 9 and 15 showed marked fluorescence. A number of samples of other fatty oils of known purity, some of which were cold-pressed from the seed in the Bureau of Chemistry, showed marked fluorescence, in some cases as marked as that of many pure mineral oils.

In order to test the delicacy of the method, a sample of kerosene, which alone showed very strong fluorescence in the light of the arc, was mixed with linseed oil No. 3. This mixture, containing 1 per cent. of kerosene, which could easily be detected by its odor, showed a slight fluorescence, but it was not so marked as that shown by linseed oil No. 4 without any addition of other oil. The pure linseed oil No. 3 was then heated to 300° C. and after cooling was found to be strongly fluorescent. The same development of strong fluorescence was observed in a sample of pure olive oil, which, before heating, showed no fluorescence. The examination of a number of turpentines demonstrated that while many of these samples show no fluorescence, some containing mineral oil also show none, and some samples of undoubted purity show marked fluorescence. It appears, therefore, that while it is interesting to know that the inclosed arc is a very

¹ "A Novel Method of Detecting Mineral Oil and Rosin Oil in Other Oils." By A. E. Outerbridge, Jr. Proceedings, Fourteenth Meeting American Society for Testing Materials.

convenient means of strongly magnifying fluorescence, this fluorescence is not proof of the presence of mineral or rosin oil.

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NITRIC NITROGEN IN MIXED FERTILIZERS.

By S. S. PECK.

Received September 5, 1911.

At the 25th annual convention of the Association of Official Agricultural Chemists, the referee on the determination of nitrogen devoted his report to the determination of nitrogen in mixtures containing nitrate of soda. In neglecting the instructions of 1906, he apologized by saying:

"Another phase of the nitrogen question considered last year and discussed in correspondence with the National Fertilizer Association seemed to outweigh in importance and urgency all others, namely, the determination of total nitrogen in mixed fertilizers to which nitrate of soda is added." In accordance with his instructions a number of determinations were made by the modified Gunning and Kjeldahl methods of mixtures, in which the source of nitrate was a solution of nitric acid, accurately standardized. The results of the different analysts showed wide variations, in the words of the author "mostly impossible." It seems very probable that the divergences were due to the heat generated by the acid and water, and Trescot expressed in his report to the referee his conviction that on dry samples, the modified Gunning method gives correct results.

In the Hawaiian Islands, about 40,000 tons of fertilizer are used annually, a large proportion of which consists of high-grade mixtures containing from 8 to 10 per cent. of nitrogen from ammonium sulphate, nitrate of soda, and organic sources, principally blood or tankage. The reliability of the modified Gunning or Kjeldahl methods is therefore of particular interest to both the fertilizer companies supplying the material and this Experiment Station, where samples of a greater part of the shipments to the plantations are analyzed. In the latter part of last year, complaints were received from a fertilizer company that even when the utmost care was observed in compounding mixtures containing nitrate, ammonia, and organic nitrogen, the analytical figures of both the company chemist and this station frequently showed a deficiency in this element. Two possible causes suggested themselves to us: first, the presence of too much moisture, and the imperfection of the Gunning method under this condition, and second, the loss of nitric nitrogen, as suggested by C. S. Cathcart.² An investigation bearing on this point was started, according to the following plan: Mixtures were made containing 3 per cent. each of nitrogen from nitrate of soda, C. P., sulphate of ammonia, C. P., and high-grade tankage, along with superphosphate and potash salts. The nitrate of soda and sulphate of ammonia were powdered and dried; the tankage was screened through a 40-mesh sieve,

only that part passing readily being used; the potash was added in one series as sulphate, in a second as muriate. The mixture contained about 8 per cent. of potash and 7.8 per cent. of phosphoric oxide soluble in water, in addition to the phosphoric oxide in the tankage, which was not determined. The ingredients were thoroughly mixed and portions weighed out as follows: Six 10-gram samples on watch glasses, and twenty-eight 2.5-gram samples on paraffined paper, on watch glasses, half of each lot containing the potash as sulphate and half as muriate. The weights of all being recorded, one each of the 10-gram and two each of the 2.5-gram lots were analyzed at once. The remainder were set aside for various intervals of time, being covered with large beakers so as to prevent contamination by dust or insects, but not hindering the free entrance of air. A further portion of each series was used for the determination of moisture according to the official method.

The 2.5-gram samples were analyzed at intervals by the modified Gunning method with the addition of 0.7 gram of mercury. A remarkable irregularity was obtained in our nitrogen figures, which we were finally able to trace to the imperfect manner in which the samples on the paraffined papers were covered by the salicylic-sulphuric acid mixture. A second set of determinations was started, with more regular results. The final figures in both sets, however, lead to the same conclusions.

The ten-gram samples were analyzed as follows: The sample was washed into a beaker and stirred in water for about an hour. It was then filtered onto a S. & S. paper, the nitrogen in a similar lot of which having been previously determined and found to be negligible in quantity. The entire sample having been transferred to the paper, it was washed until the entire leadings amounted to 500 cc. The residue was then dried at a low temperature, and digested with mercury, sulphuric acid, and sulphate of potash. The nitrogen constituted the residual organic nitrogen.

Twenty-five cc. portion of the leadings were respectively distilled with caustic soda for ammonia nitrogen, and reduced with iron and sulphuric acid for the nitric and ammonia nitrogen, according to the Ulsch-Street method. A like quantity was pipetted into a 500 cc. Kjeldahl digestion flask, treated with iron and sulphuric acid to reduce the nitric nitrogen to ammonia, and then digested with sulphuric acid, mercury and potassium sulphate according to the usual Kjeldahl method. Considerable difficulty is met here, since anhydrous salts or double salts of iron as sulphate are precipitated and cause considerable bumping. The digestion is completed in about two hours, as there is really very little organic nitrogen present. Distillation presented the same difficulties as regards bumping, until we resorted to the use of copper distilling flasks, since when we have had no other trouble except the uncertainty as to when the large quantity of acid present is neutralized by the soda lye. The distillate represents the nitrogen as ammonium, nitrate and soluble organic; this added to the residual organic gives the total nitrogen. One

¹ Bull. 122, Bureau of Chemistry, U. S. Department of Agriculture.

² This JOURNAL, Jan., 1911.

error which enters into our results is that in distilling both for ammonia nitrogen and in the Ulsch-Street method, using soda-lye, a certain amount of organic nitrogen is recorded as ammonia nitrogen. This, as will be shown later, amounts to only a very small percentage. Another error for which we have not corrected is the nitrogen in a blank. This may amount to as much as 0.1 per cent. in a 9 per cent. sample, but this correction has not been made since it in no wise interferes with our results used from a comparative standpoint; the difference must be the same in all determinations.

The results of our analyses are tabulated herewith:

SERIES A.—POTASH AS SULPHATE.

Time.	Gunning.		New method						
	Moisture.	Nitrogen.	Moist.	Ammonia.	Nitric.	Total water soluble Nitrogen.	Organic residue.	Organic.	Total.
0 week...	4.6	9.07	4.6	3.11	3.14	6.53	2.56	2.84	9.09
1 week...	14.1	8.98
2 weeks..	7.3	9.06
4 weeks..	15.4	8.93	10.4	3.17	3.12	6.50	2.57	2.78	9.07
16 weeks..	13.7	8.62	13.9	3.08	3.11	6.55	2.60	2.96	9.15

SERIES B.—POTASH AS MURIATE.

0 week...	5.4	8.99	5.4	3.08	3.08	6.47	2.57	2.88	9.04
1 week...	30.9	8.58
2 weeks..	31.1	8.64
4 weeks..	35.3	8.61	20.5	3.08	3.17	6.49	2.58	2.82	9.07
16 weeks..	38.0	8.42	37.6	3.07	3.01	6.43	2.62	2.97	9.05

The moisture figures are given as percentages on dry matter. The moisture in the original sample was determined by drying; that in the other samples was calculated from the increase in weight. The percentages of nitrogen are reported in terms of the original material.

Series B increased in moisture considerably more than Series A, and there is a greater apparent loss in nitrogen, on the basis of the analyses by the Gunning method. The other method, however, shows that this loss is only apparent, and due to the imperfections of the Gunning method when applied to wet material. Each of the Gunning figures is the average of three determinations, the results of which were fairly concordant.

The average of the six determinations by the new method gives the following results:

Nitrogen as ammonia.....	3.095
Nitrogen as nitrate.....	3.105
Nitrogen as organic.....	2.875
Nitrogen total.....	9.075

In a separate determination with the tankage alone, it was found that on distilling that soluble in water with soda-lye in the usual amounts employed, there was recovered as ammonia, nitrogen amounting to 2.8 per cent. of the total nitrogen in the material. This would necessitate a correction in the above figures of 0.08 per cent. in the ammonia, making a true average result of 3.015 per cent. nitrogen as ammonia and 2.955 per cent. organic nitrogen.

In addition to these determinations, fertilizer samples showing a deficiency in total nitrogen, and containing the three forms of this element, have been re-

analyzed by both the modified Gunning (with the addition of mercury) and the new method. In these instances, with one exception, the phosphoric oxide was present as insoluble lime phosphate, and in all, the potash was in the form of sulphate.

The results were as follows:

Moisture.	Gunning.	New method.	Guarantee.
6.41	8.82	8.86	9
7.58	8.93	8.95	9
9.08	9.63	9.74	10
13.58	9.69	9.97	10
8.65	8.37	8.69	9
11.69	9.48	9.75	10
7.39	7.90	7.89	8

We interpret our results to signify that in the presence of sufficient moisture, the modified Gunning method gives incorrect results, and that a mixed fertilizer containing nitrate of soda and acid phosphate does not even after a lapse of four months lose any nitrogen. On arriving at this last conclusion, we believe that we have avoided two errors inherent in Cathcart's method of investigation: (1) the unreliability of the modified Gunning method in the presence of much moisture, and (2) the uncertainty of moisture determinations in such a complex as a mixed fertilizer, with the unreliability of such a basis for comparative purposes, a point which has already been emphasized in *THIS JOURNAL*.¹

The larger part of the analytical work performed in obtaining data for this article was made by Mr. A. E. Jordan.

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THE OIL OF DOUGLAS FIR: A PRELIMINARY STUDY OF ITS COMPOSITION AND PROPERTIES.

By H. K. BENSON AND MARC DARRIN.
Received September 21, 1911.

In the steam distillation of resinous Douglas Fir wood, a crude greenish yellow turpentine of syrupy consistency is obtained. In the distillation process as practiced in the Pacific Northwest, steam under a boiler pressure of 45 to 60 abs. is used, and the retorts are usually placed under a diminished pressure at the end of the distillation period for the purpose of removing the last traces of oil from the wood chips.

The yield of this crude turpentine per cord is dependent upon the degree of pitchiness or "fatness" of the wood, but in the case of selected mill waste and stump wood, it ranges from 5 to 7 gallons per cord. When redistilled under low pressure steam, this yields from 4 to 5 gallons of a water-white turpentine which has a good odor and complies with the requirements for spirits of turpentine as established by the U. S. Bureau of Chemistry in *Bulletin 109*, revised, Bureau of Chemistry, U. S. Dept. of Agriculture.

The residue after the removal of the turpentine consists of a clear viscous, yellow oil, similar in appearance to the pine oil obtained from the refining of the steam turpentine from Norway and of Michigan and long leaf pine of the south.

¹ October, 1909, Editorial.

The latter has been studied by Walker¹ and by Teeple² with conclusions reached in each case that the essential constituent of pine oil is terpineol. Inasmuch as the residual oil from the turpentine distillation of fir wood seemed similar both as to its production and general appearance and especially since the manufacturers could not dispose of it on account of the oil having to go on the market as fir oil, it seemed desirable to investigate its composition and properties. The present investigation is merely preliminary to a more complete examination of its uses and commercial applications now in progress.

The material consisted of several gallons of the oil from a commercial plant operating in the manner above described. The first effort in studying its properties consisted in a determination of its constants, the following being the mean of a number of determinations:

TABLE OF CONSTANTS OF FIR OIL.

Color.....	light yellow.
Rotation $[\alpha]_D^{20}$	37.6° laevo.
Refractivity at 20° C.....	1.4818.
Solubility in 70% alcohol.....	49 oil in 100 alcohol.
Acid number.....	1.55.
Saponification number.....	11.1.
Iodine number.....	185.0
Melting point (by solid CO ₂).....	below 40° C.

The constants for pine oil are described by Teeple,³ as follows:

Color.....	faint yellow color.
Sp. gr.....	0.935 to 0.947.
Rotation $[\alpha]_D^{20}$	11° laevo.
Refractivity.....	1.4830.
Boiling point.....	Begins at 206° C. 75% distilling between 211°-218° C.

Examination was next directed along the line of a possible isolation of its main constituents. For this purpose, one liter of fir oil was subjected to repeated fractional distillations and constants determined for each fraction:

CONSTANTS FOR OIL OF DOUGLAS FIR FRACTIONS

Fraction.	Per cent. of total by wt.	Color.	Sp. gr. at 20° C.	Laevo rotation $[\alpha]_D^{20}$	Index refrac- tion 20° C.
Fir oil.....	..	yellow	0.936	-37.6°	1.4818
175-206° C.....	4.8	yellow	0.890	-42.5°	1.4745
206-208° C.....	0.3	yellow	1.4820
208-210° C.....	0.6	yellow	1.4750
210-212° C.....	2.2	almost white	..	-40.2°	1.4815
212-214° C.....	4.3	almost white	0.930	-40.1°	1.4810
214-216° C.....	5.4	almost white	0.932	-40.1°	1.4810
216-218° C.....	5.9	almost white	0.936	-40.5°	1.4800
218-220° C.....	17.1	almost white	0.940	-43.1°	1.4800
220-222° C.....	15.6	yellow	0.940	-45.2°	1.4815
222-224° C.....	7.5	yellow	0.940	-46.1°	1.4830
224-226° C.....	5.9	yellow	0.940	-46.1°	1.4840
226-228° C.....	1.6	yellow	0.940	-44.0°	1.4850
228-230° C.....	0.6	yellow	1.4855
230-260° C.....	2.7	bright yellow	0.944	-35.9°	1.4880
Residue.....	10.0	black	0.988
Water.....	10.0
Loss.....	5.5

Interpretation of Results of Fractional Distillation:
The boiling point varies between 175-260° C.,

¹ Massachusetts Institute of Technology Bulletin, Sept., 1905.

² J. Am. Chem. Soc., 30, 412.

³ Loc. cit.

57.4 per cent. distilling between 214-226° C. and 33 per cent. 218-222° C., yielding products with similar physical constants. This latter fraction represents the chief constituent of fir oil and to which its properties are mainly due. Further examination of the physical constants shows that the oil is not of a simple nature but represents a mixture of a complex character.

Percentage Composition:

A number of analyses were made of the oil and the mean results are as follows:

Hydrogen.....	11.9%
Carbon.....	76.0%
Oxygen.....	12.1
Nitrogen.....	00.0%
Halogen.....	00.0%
	100.0%

Terpin Hydrate.—The oxygen content of the oil indicated the presence of an oxygenated terpene, and an attempt was made to ascertain its behavior toward oxidizing agents, such as are used in the preparation of terpin hydrate from terpenes.

1. The fir oil was treated with nitric acid and alcohol in refrigerator. At the end of one week the solution turned deep brown, but no crystals had separated. At the end of one month, the solution had turned black and formed a very viscous-like tar and possessed a very strong camphor odor. Well-formed, colorless crystals of the hydrate had formed, m. p. 117° C. Yield of terpin hydrate, 13 per cent. of fir oil. The remaining oil was subjected to a continued steam distillation and yielded a small amount of a clear, slightly yellow oil with a camphor-like odor. This was probably due to an oxidation product of the oil by the nitric acid.

2. Fir oil was hydrolyzed with 5 per cent. sulphuric acid at ordinary temperature. At the end of a week, the oil layer was filled with a multitude of clear, radiating, needle-like crystals. These crystals kept slowly growing until, at the end of the second week, they covered the bottom of the dish. M. p. of crystals 117-118° C.

Tests for Ketones.—Separate samples of fir oil were treated with saturated solutions of (a) sodium bisulphite and (b) ammonia, for a period of one month. In neither case were there indications of crystalline derivations—tending to show the oxygen found by analysis was *not* of an aldehydic or ketonic nature.

From a study of the above data, the authors conclude that fir oil owes its properties to the presence of terpineol. This conclusion is based on a number of considerations. The double ethylene bond readily accounts for the high iodine absorption. The agreement of the percentage composition with terpineol (H, 11.7; C, 78.0; O, 10.3) is strikingly close when the presence of other constituents is considered. The ease by which terpin hydrate is formed from fir oil by the action of dilute sulphuric acid strongly indicated terpineol, since the latter is an intermediate product in the formation of a terpin from a terpene. The constants for terpineol are as follows:

Boiling point at 760 mm.....	217-218° C. ¹
Sp. gr. at 15°.....	0.935-0.940 ¹
Refractivity n_D^{20}	1.48084 ¹
Melting point.....	35° ²

The close agreement of the fir oil and especially of the fractions between 218-220° is very marked, with the exception of the melting point, the fir oil solidifying below -40° C. and the fractions between 218-220° at 0° C. This exception is not unusual in the presence of impurities, as it has been shown by Bouchardat and Voiry³ that terpineol which will not solidify above -50° C. has a melting point of 30-32° C.

The conclusion drawn from these tests is that not less than $\frac{1}{3}$ of fir oil consists of terpineol and that fir oil is so closely similar to pine oil in its properties as to be able to be substituted for the latter in its commercial application.

The uses of the latter have become very extensive in the last few years. As a solvent for varnish gums in the cold, for rubber, for nitrocellulose lacquer, in the manufacture of metal polishes and for general use as an essential oil, it is being sold regularly in carload lots. This same market should be open in the future to fir oil for the same or similar uses.

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A STUDY OF THE BROMINE AND IODOMETRIC METHODS FOR THE DETERMINATION OF RESORCINOL.⁴

By C. M. PENCE.

Received August 28, 1911.

Koppeschaar's (1) modification of Landolt's bromine method for the determination of phenol suggested several years ago that other phenols (2, 3, and 4) might be estimated by practically the same procedure.

Degener (5) devised the following bromine method for resorcinol: A standard solution of free bromine is run into the resorcinol solution as long as a precipitate forms and until solution becomes yellow. Then potassium iodide is added and the liberated iodine titrated with $N/10$ thiosulphate.

Richards (6) proposed an iodometric method similar in procedure to the bromine method of Degener with the exception that it is necessary to add some substance like sodium acetate to cause greater completion of the reaction by uniting with the hydriodic acid formed during the substitution.

A study was made of these two methods with the purpose of finding a rapid and yet accurate method for the estimation of resorcinol.

Resorcinol of uncorrected m. p. 109-110° C. was recrystallized from distilled water, the crystals were disintegrated and allowed to drain thoroughly, then recrystallized from absolute alcohol free from aldehydes, etc. The crystals thus obtained were broken

apart, thoroughly drained, desiccated in vacuum desiccator over sulphuric acid, powdered and re-desiccated to free from the last traces of alcohol.

Volumetric solutions were prepared from these crystals and an attempt was made to apply the Koppeschaar procedure for the volumetric estimation of phenol as outlined in the U. S. Pharmacopoeia, 1900 ed. This method seemed to have several advantages over that of Degener inasmuch as the Koppeschaar-bromine solution is much superior to a standard solution of free bromine in stability and ease of handling.

The U. S. P. of Koppeschaar method is briefly as follows: The aqueous phenol solution is measured with a pipette into a 500 cc. receptacle with ground-glass stopper. A measured quantity of standard bromine solution sufficient to give a small excess of bromine is added, then 5 cc. of concentrated HCl. The bottle is shaken and let set 30 minutes. Five cc. of 20 per cent. KI are added and bottle shaken. One cc. of CHCl_3 is added, bottle again shaken and free iodine titrated with $N/10$ thiosulphate until chloroform is free from color. Starch was used as an indicator instead of chloroform, which was added merely as a solvent for precipitated phenols, thus increasing the sensitiveness of end point.

It was found that when solution was allowed to stand 30 minutes after addition of HCl the results would be much too high. This was attributed to the formation of tribromoresorcinolbrom (7) which did not readily decompose after the addition of KI. Expts. 1 and 2 show this tendency, Expt. 2 also showing that short time of standing after addition of KI did not permit the decomposition of the additive compound formed.

An attempt was now made to counteract tendency for formation of this compound by shortening the reaction period of bromine upon resorcinol. Expts. 3, 4 and 5 show much lower results.

In the next experiments (6-14) the reaction period of bromine was kept at 1 min. and solution was allowed to stand after the addition of KI. It was found that KI caused a reversal whereby the tribromoresorcinolbrom was entirely decomposed. Expts. 6 and 7-12 and 14 show this reversal effect of KI and length of time required for complete reversal under the specific experimental conditions used. Expt. 13 shows that heat increases the speed of reversal.

Now it was observed during the course of the above experiments that a pronounced precipitate formed upon the addition of KI. It was thought probable that this precipitate consisted partially of or occluded some tribromoresorcinolbrom and prevented a ready reversal. This supposition was verified by Expts. 15-28. By proper dilution the precipitation was prevented. However, it was found that reversal did not cease after breaking down the tribromoresorcinolbrom but that some of the tribromoresorcinol was decomposed. Chloroform was used, thinking that decomposition might be taking place almost entirely during the titration. This was found to be untrue (Expts. 20, 24, 25, 26, 27, 28). Nevertheless, these experiments did show that amount of reversal was

¹ Gildermeister and Hoffman, p. 140.

² Liebig's Ann., 275, p. 104.

³ Compt. rend., 104, 996; Ber., 20, 286.

⁴ Paper read before the Pharmaceutical Division, Indianapolis meeting, Amer. Chem. Soc., June, 1911.

Expt.	Resorcinol. cc.	BrN/10. cc.	H ₂ O. cc.	HCl. cc.	Time standing.	H ₂ O. cc.	KI 20 per cent.	Time standing.	H ₂ O. cc.	Procedure.	Time standing.	CHCl ₃ cc.	Result Per cent.	Br N 19 excess.
1	20	50	50	5	30 min.	...	10	5	102.58	...
2	20	50	30	5	60 "	200	5	10 min.	102.6	...
3	20	50	30	5	5 "	...	10	...	200	20	100.13	...
4	20	50	30	5	5 "	200	10	100.15	...
5	20	50	30	5	5 "	...	5	...	200	100.1	...
6	10	20	...	5	1 "	...	10	1 hr.	150	10	100.3	1.5
7	10	20	...	5	1 "	...	10	2 hrs	150	10	99.9	1.7
8	20	50	20	5	1 "	...	10	2 "	150	10	99.78	...
9	20	50	20	5	1 "	...	10	2 "	150	10	99.71	...
10	50	40	10	5	1 "	...	10	1 hr.	150	10	99.89	8.25
11	50	40	10	5	1 "	...	10	1 "	150	10	99.94	8.22
12	20	20	20	5	1 "	...	10	30 min	150	10	100.39	1.42
13	20	20	20	5	1 "	...	10	30 "	150	10	99.82	1.6
14	20	20	20	5	1 "	...	10	1 hr.	150	10	99.99	1.48
15	20	50	30	5	1 "	...	10	1 "	250	Shook well	1 min.	...	99.4	about 12.0 cc.
16	20	50	30	5	1 "	...	10	...	250	"	1 "	...	99.3	"
17	20	50	30	5	1 "	...	15	...	250	"	5 "	...	99.41	"
18	20	50	30	5	1 "	...	15	...	250	"	1 hr.	...	99.4	"
19	20	50	30	5	1 "	...	10	1 hr	200	"	1 min	...	99.4	"
20	20	50	30	5	2 "	...	10	1 "	200	"	1 min	20	99.5	"
21	20	50	30	5	5 "	...	10	5 min.	200	"	2 "	20	99.6	"
22	20	50	30	5	5 "	...	10	5 "	200	"	2 "	20	99.56	"
23	20	50	30	5	5 "	...	10	5 "	200	"	2 "	...	99.59	"
24	20	50	30	5	2 "	...	10	1 hr.	200	"	1 "	20	99.5	"
25	20	50	30	5	1 "	...	10	2 min.	200	"	...	20	99.76	"
26	20	50	30	5	1 "	...	10	2 "	200	"	...	20	99.74	"
27	20	50	30	5	1 "	...	10	1 "	200	"	...	20	99.74	"
28	20	50	30	5	1 "	...	10	1 "	200	"	...	20	99.76	"
29	20	50	30	5	5 "	...	5	1 hr.	200	"	99.30	"
30	25	50	50	5	1 "	...	5	1 "	200	"	99.25	"
31	25	50	50	5	1 "	200	5	"	20 "	...	99.95	"
32	20	50	50	5	2 "	200	5	"	15 "	...	99.92	"
33	20	50	30	5	2 "	200	5	"	30 "	...	99.92	"
34	25	50	50	5	1 "	200	5	1 hr.	...	"	99.49	"
35	25	50	50	5	1 "	200	5	1 "	...	"	99.45	"
36	20	50	30	5	2 "	...	5	3 min.	200	Shook well	1 min.	...	100.00	"
37	20	50	30	5	5 "	...	5	6 "	200	"	1 "	...	100.00	"
38	20	50	30	5	5 "	...	5	5 "	200	"	1 "	...	99.96	"
39	20	50	30	5	5 "	...	5	3 "	200	"	1 "	...	99.86	"
40	20	50	30	5	5 "	...	5	5 "	200	"	1 "	...	100.0	"
41	20	50	30	5	1 "	...	10	...	200	"	...	20	99.86	"
42	20	50	30	5	2 "	...	10	...	200	"	...	20	100.05	"
43	20	50	30	5	1 "	...	5	...	200	"	100.1	"
44	20	50	30	5	3 "	...	5	...	200	"	1 min	...	100.21	"
45	20	50	30	5	5 "	...	5	...	200	"	1 "	...	100.4	"
46	20	50	30	5	1 "	200	5	"	10 "	...	100.03	"
47	20	50	30	5	30 "	200	5	"	45 "	...	99.93	"
48	20	50	30	5	30 "	200	5	"	15 "	...	100.1	"
49	20	50	30	5	45 "	200	5	"	1 hr.	...	100.1	"
50	20	50	30	5	15 sec.	200	5	"	1 min.	...	99.7	"
51	25	50	30	5	1 min.	200	5	"	1 "	...	101.04	34.6 cc.
52	25	50	30	5	1 "	200	5	"	3 "	...	100.26	34.9 cc.
53	20	50	30	(10 cc. 10%)	1 "	200	5	1 min.	99.86	...
54	25	50	50	5	1 "	200	5	Shook well	1 min.	...	99.95	about 16.0 cc.
55	25	50	50	5	1 "	200	5	"	3 "	...	99.95	"
56	25	50	50	5	1 "	200	5	"	8 "	...	99.97	"
57	25	50	50	5	1 "	200	5	"	14 "	...	99.95	"
58	25	50	50	5	1 "	200	5	"	5 "	...	100.00	"
59	25	50	50	5	1 "	200	5	"	8 "	...	100.12	"
60	25	50	50	5	1 "	200	5	"	12 "	...	100.04	"
61	25	50	50	5	1 "	200	5	"	15 "	...	100.04	"
62	25	50	50	5	1 "	200	5	"	20 "	...	99.99	"

Exp	Resorcinol. cc.	N/10 I. cc.	NaCH ₂ COO. Grams.	Na ₂ HPO ₄ . Grams.	NaHCO ₃ . Grams.	Time standing.	H ₂ O added. cc.	Result, after excess thiosulphate, titrated back	Remarks
63	20	50	...	2	...	5 min.	200	...	Too dark to titrate
64	20	50	1	1 hr.	200	99.2	98.94
65	20	50	1	15 min.	200	98.6	98.35
66	20	50	1	at once	200	98.4	98.7
67	20	50	1	30 min	200	99.33	99.15
68	20	50	1	at once	200	99.33	99.15
69	20	50	5	at once	200	97.7	97.5
70	20	50	2	at once	200	98.2	98.3
71	20	50	5	3 hrs	200	...	Too dark to titrate
72	20	50	0.5	5 min	200	...	Too dark to titrate
73	20	50	2.0	3 hrs	200	...	Too dark to titrate

dependent upon time of standing after dilution. Compare Expts. 15-24 with Expts. 25-28.

It now remained to ascertain whether or not a smaller amount of KI would counteract tendency for decomposition of tribromoresorcinol and under what conditions such would obtain. It was found that this decomposition was prevented; that solution must not stand too long after addition of KI before dilution; that in diluted condition, time of standing might be somewhat prolonged without deleterious results; that after dilution and addition of KI, solution should not stand as long as 1 hour before titration (Expt. 29 and 30-31, 32, 33-34, 35).

Several experiments were run varying the length of time bromine was allowed to react with resorcinol in order to study the length of time it would take KI to produce proper reversal under varying conditions. In general, it may be said that KI should react at least as long as bromine is permitted to react with resorcinol. Experiments 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48 and 49.

It was found in Expt. 50 that reaction between bromine and resorcinol would not be completed in 15 secs.; in Expts. 51 and 52 that solution should set at least 5 mins. after addition of KI when excess of bromine is large; in Expt. 53 that reaction between bromine and resorcinol solutions is much more rapid when strong acid is used.

The method of Degener would be open to considerable error, due to formation of the additive compound and to insufficient time and dilution for its decomposition.

Richards' iodometric method has several features that condemn it: 1st, solutions darken upon standing so that end point is obscured; 2nd, even upon prolonged standing results are much too low (Expts. 63-73).

The following method is suggested for the estimation of resorcinol in commercial resorcinol: Its accuracy may be noted by reference to Expts. 54-62.

Weigh out 1.4563 g. resorcinol. Dissolve in distilled water, filter if necessary, and dilute to 500 cc. in a volumetric flask. Withdraw a 25 cc. portion with a pipette and place in a 500 cc. receptacle with ground-glass stopper. Add 50 cc. *N*/10 bromine solution and 50 cc. dist. water. Add 5 cc. conc. HCl, shake and let set about 1 minute. Dilute with about 200 cc. water, add 5 cc. 20 per cent. KI, shake vigorously and let set about 5 minutes. Titrate, using starch as indicator. Divide number of cc. of *N*/10 bromine solution consumed by 0.4 (or multiply by 2.5) for correct percentage of resorcinol.

A blank should be run along with the determination, using the same pipette and draining in the same manner in order to obtain an exact duplicate titre of *N*/10 bromine solution. 7-10 cc. of 20 per cent. KI should be used instead of 5 cc. as in regular determination.

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A NEW AND ACCURATE METHOD FOR DETERMINING THE TRYPTIC VALUE OF PANCREATIN.¹

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At the present time very little attention is being paid to pancreatin as regards its proteolytic activity. This is probably due to the fact that no satisfactory test has been proposed by which it might be ascertained just how much proteid a given sample of pancreatin will digest.

The tryptic value of pancreatin should be taken into account for it is more energetic than pepsin. In the case of pepsin considerable time is necessary for proteid to be converted into peptone while trypsin converts proteids rapidly into proteoses and peptone. It has been stated that trypsin is so energetic that it will convert proteid beyond the stage of peptone into leucin, tyrosin, and other amides.

The U. S. P. method for determining the tryptic power of pancreatin is very indefinite and uncertain because of the manner of testing the end reaction. It states that by adding a little nitric acid to a portion of the peptonized milk no coagulation should occur. As regards the word coagulation in this test there is a difference of opinion. If we are to think of coagulation as the result obtained when adding rennin to milk it would be better to call this separation a precipitation. The result depends altogether upon the amount of acid added. If a minute quantity of acid is added, no precipitate is formed, while with more acid there is a decided precipitation. A large excess of acid generally results in solution of the precipitate. Acid will cause a precipitation in peptonized milk no matter how long the digestion takes place.

In view of the importance of trypsin in pancreatin the writer wishes to propose a milk test which, if carried out exactly in accordance with directions, will give very accurate results. In testing the activity of enzymes, it is very important to adhere to certain conditions such as temperature, time for digestion, etc. So it is in testing trypsin. This test determines the amount of pancreatin necessary to peptonize a given quantity of milk in fifteen minutes. The end reaction is determined by adding a slightly acidified solution of rennin to a portion of the peptonized milk and noting if precipitation or coagulation takes place. The final end point of the test is reached when the milk is just sufficiently peptonized so that it will not be coagulated by the rennin. To determine this it is necessary to test the pancreatin first at wide

¹ Paper read before the Pharmaceutical Division, June meeting, American Chemical Society.

ranges of strength, say 1 to 700, 1 to 800, 1 to 900, etc. By this is meant 1 gram of pancreatin to 700 cc. of milk. After it is found between what wide ranges the strength of the pancreatin lies, a second series of tests are made at intermediate values until the exact strength of the pancreatin is found. In carrying out the test it was found necessary to make the milk slightly alkaline with sodium bicarbonate to prevent the pancreatin from curdling the milk. This coagulation is probably due to the presence of an enzyme in pancreatin similar to rennin.

The materials required for the test are as follows:

0.5 gram pancreatin added to sufficient distilled water to make 50 cc. of solution.

900 cc. of milk containing 1.8 grams of sodium bicarbonate.

2 grams of rennin (1:30,000 in 10 minutes or equivalent) and 1 cc. of 6 per cent. acetic acid (U. S. P.) added to 50 cc. of distilled water.

After warming the milk, place exactly 50 cc. in a cylindrical tube of about 100 cc. capacity. Prepare several such tubes and place in a water bath maintaining the temperature at 40 degrees C. Add to the tubes of milk the following amounts of the pancreatin solution:

cc.	
8.33	(1:600)
7.69	(1:650)
7.14	(1:700)
6.66	(1:750)
6.25	(1:800)

In each case note the exact time when the pancreatin is added, mix well and after digesting fifteen minutes place 5 cc. of the digested milk in a test tube, add 3 cc. of the rennin solution and shake well. No precipitate indicates that the casein has all been peptonized and that the pancreatin is stronger than the strength tested. For example if there was no precipitation at 1:700, but there was a precipitation at 1:750, then it would be necessary to run more digestions between 1:700 and 1:750. Make a fresh solution of pancreatin and use the following amounts:

cc.	
7.04	(1:710)
6.94	(1:720)
6.84	(1:730)
6.75	(1:740)

In this manner it can be determined quite accurately how many times its own weight of milk a given sample of pancreatin will peptonize. In order to get accurate results the test must be carried out strictly in accordance with directions. As stated above acid will precipitate peptonized milk, therefore, just enough acid is added to the rennin solution so that 3 cc. of this solution will neutralize the sodium bicarbonate in 5 cc. of the peptonized milk. Then the rennin will do its work, for it will not form the precipitate in an alkaline solution.

Attention must be called to the fact that pancreatin in a neutral solution deteriorates quite rapidly. Therefore this solution should be made up the last thing so it can be added immediately to the milk. The amount of pancreatin solution suggested is sufficient for testing the strengths as indicated.

It must be borne in mind that all tests of this nature are purely arbitrary; consequently a slight variation in the carrying out of such a test would give different results. The method gives accurate results to within two, or three per cent. which is closer than pepsin can be tested on egg albumen and equal to the accuracy of the starch methods for testing diastases. If this proposed test is carried out as indicated it will undoubtedly prove very satisfactory and will make it possible for one to know the exact proteolytic activity of a sample of pancreatin.

In testing various commercial samples of pancreatin by the above test the following results were obtained:

No.	
1	1:280
2	1:120
3	1:130
4	1:670
5	1:850
6	1:1450
7	1:1750
8	1:1200
9	1:960

It will be noted that there is a wide variation in the tryptic value of commercial pancreatins. The writer suggests if the above test meets with favor in the hands of other workers, it may serve as the basis for the official assay of the U. S. P. From the above examination of commercial pancreatins it would appear that a requirement of 1 to 800 or 1 to 1000 would be a fair standard.

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DETROIT.

THE ACCELERATING ACTION OF HCl UPON THE STARCH-CONVERTING PROPERTIES OF PANCREATIN AND MALT.¹

By A. ZIMMERMAN.

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A pancreatin of such strength that one part will convert 25 parts of corn starch can be so accelerated that one part will convert 125 parts of corn starch and 250 parts of potato starch in 5 minutes. This acceleration of the starch converting action of pancreatin is accomplished by extremely small quantities of HCl, which are added when making the starch paste. The proportion of acid used is so small that it absolutely does not convert any starch into glucose, for the proportion necessary to do this would destroy the pancreatin. The temperature at which the conversion takes place is important; when the pancreatin is added to the starch paste the latter should be at 135° F. The pancreatin is added in solution at 70° F. (no higher), so that the temperature after the addition of the pancreatin to the starch paste is about 125° F. (not lower).

The quantity of HCl necessary is $\frac{1}{10}$ of one per cent., absolute acid, of the weight of the starch.

The starch paste consists of one part of starch to 16 parts of water, the HCl being added to the water before the addition of the starch. The mixture is then

¹ Paper read before the Pharmaceutical Division, June meeting of the American Chemical Society, Indianapolis.

COMPARATIVE DIASTATIC ACTION OF PANCREATIN AND MALT

Pancreatin, 1 to 25 and 1 to 35 starch test U. S. P.

Corn starch..... 3.75 grams
 Water..... 60 cc.
 Hydrochloric acid, N/10..... 1 cc.

Pancreatin, 1 to 25..... 0.030 gram

Converts in 5 minutes

Temp. 135° F., one panc. to 125 starch

Corn starch..... 1.875 grams
 Water..... 60 cc.
 Hydrochloric acid, N/10..... 0.5 cc.

Pancreatin, 1 to 25..... 0.015 gram

Converts in 5 minutes

Temp. 135° F., one panc. to 125 starch

Corn starch..... 3.75 grams
 Water..... 60 cc.
 Hydrochloric acid, N/10..... 0.5 cc.

Pancreatin, 1 to 25..... 0.021 gram

Converted in 5 minutes

Temp. 135° F., one panc. to 175 starch

Corn starch..... 3.75 grams
 Water..... 60 cc.
 Hydrochloric acid, N/10..... 2/3 cc.

Pancreatin, 1 to 25..... 0.021 gram

Converted in 5 minutes

Temp. 135° F., one panc. to 175 starch

Corn starch..... 3.75 grams
 Water..... 60 cc.
 Hydrochloric acid, N/10..... 1/3 cc.

Pancreatin, 1 to 25..... 0.021 gram

Converts in 10 minutes

Temp. 135° F., one panc. to 175 starch

Corn starch..... 3.75 grams
 Water..... 60 cc.
 Hydrochloric acid, N/10..... 2.5 cc.

Pancreatin, 1 to 35..... 0.021 gram

Converted in 5 minutes

Temp. 135° F., one panc. to 175 starch

Corn starch..... 1.875 grams
 Water..... 60 cc.
 Hydrochloric acid, N/10..... 2 cc.

Pancreatin, 1 to 25..... 0.015 gram

Converted in 35 minutes

Temp. 135° F., one panc. to 125 starch

Potato starch..... 3.75 grams
 Water..... 60 cc.
 Hydrochloric acid, N/10..... 1 cc.

Pancreatin, 1 to 25..... 0.015 gram

Converted in 5 minutes

Temp. 135° F., one panc. to 250 starch

Potato starch..... 3.75 grams
 Water..... 60 cc.
 Hydrochloric acid, N/10..... 2 cc.

Pancreatin, 1 to 25..... 0.015 gram

Converted in 5 minutes

Temp. 135° F., one panc. to 250 starch

Potato starch..... 7 grams
 Water..... 120 cc.
 Hydrochloric acid, N/10..... 2 cc.

Pancreatin, 1 to 35..... 0.021 gram

Converted in 5 minutes

Temp. 135° F., one panc. to 350 starch

Corn starch..... 3.75 grams
 Water..... 60 cc.
 Sulphuric acid, N/10..... 1 cc.

Pancreatin, 1 to 25..... 0.030 gram

Converted in 50 minutes

Temp. 135° F., one panc. to 125 starch

Corn starch..... 3.75 grams
 Water..... 60 cc.
 Tartaric acid, N/10..... 3 cc.

Pancreatin, 1 to 25..... 0.30 gram

Converted in 30 minutes

Temp. 135° F., one panc. to 125 starch

Corn starch..... 3.75 grams
 Water..... 60 cc.
 Pancreatin, 1 to 25..... 0.030 gram

Boric acid (6.3 grams to liter)..... 3 cc.

Converted in 30 minutes

Temp. 135° F., one panc. to 125 starch

Corn starch..... 3.75 grams
 Water..... 60 cc.
 Pancreatin, 1 to 25..... 0.15 gram

Converts in 5 minutes

Temp. 104° F., one panc. to 25 starch

Malt infusion 1 in 6 acidity (as lactic acid) 0.35 per cent.

Corn starch..... 3.75 grams

Water..... 60 cc.

Malt infusion..... 10 cc.

Converts in 5 minutes

Temp. 135° F., one malt to 2 1/4 starch

Corn starch..... 3.75 grams

Water..... 60 cc.

Malt infusion, made neutral..... 20 cc.

Converts in 5 minutes

Temp. 135° F., one malt to 1.15 starch

Corn starch..... 3.75 grams

Water..... 60 cc.

Hydrochloric acid, N/10..... 1 cc.

Malt infusion..... 4 cc.

Converts in 5 minutes

Temp. 135° F., one malt to 5 7/10 starch

Corn starch..... 3.75 grams

Water..... 60 cc.

Malt infusion..... 4 cc.

Hydrochloric acid, N/10..... 2 cc.

Converts in 5 minutes

Temp. 135° F., one malt to 5 7/10 starch

Corn starch..... 3.75 grams

Water..... 60 cc.

Hydrochloric acid, N/10..... 1 1/2 cc.

Malt infusion..... 4 cc.

Converts in 10 minutes

Temp. 135° F., one malt to 5 7/10 starch

Potato starch..... 3.75 grams

Water..... 60 cc.

Malt infusion..... 5 cc.

Converted in 5 minutes

Temp. 135° F., one malt to 4 1/2 starch

Potato starch..... 3.75 grams

Water..... 60 cc.

Hydrochloric acid, N/10..... 2 cc.

Malt infusion..... 4 cc.

Converted in 5 minutes

Temp. 135° F., one malt to 5 7/10 starch

Corn starch..... 3.75 grams

Water..... 60 cc.

Sulphuric acid, N/10..... 1 cc.

Malt infusion..... 4 cc.

Converted in 10 minutes

Temp. 135° F., one malt to 5 7/10 starch

Corn starch..... 3.75 grams

Water..... 60 cc.

Tartaric acid, N/10..... 1 cc.

Malt infusion..... 4 cc.

Converted in 10 minutes

Temp. 135° F., one malt to 5 7/10 starch

Corn starch..... 3.75 grams

Water..... 60 cc.

Boric acid (6.3 grams to one liter)..... 2 cc.

Malt infusion..... 4 cc.

Converted in 10 minutes

Temp. 135° F., one malt to 5 7/10 starch

The starch paste was prepared using $3\frac{3}{4}$ grams starch to 60 cc. water.

The commercial starch contains about 16 per cent. moisture.

The pancreatin was added to the starch paste when the temperature of the latter was 130° F., which fell to 110° F., at which temperature the digestion was continued.

One gram anhydrous starch equals 1.055 grams maltose.

These tables by comparison indicate that by acceleration of pancreatin it can be made a cheaper starch converter than malt is.

The malt infusion was added to the starch paste when the temperature of the latter was 130° F., which fell to 110° F., at which temperature the digestion was continued.

The reducing substances in the malt infusion were estimated and calculated as maltose 0.105 gram to 1 cc. of malt infusion, and subtracted from the total reduction by the copper, to obtain the actual amount of maltose formed from the starch by the malt.

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DETERMINATION OF MALIC ACID.¹

By P. B. DUNBAR AND R. F. BACON.

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INTRODUCTION.

The method described herein is based on the fact first observed by Walden² that under certain conditions uranium salts produced a very marked increase in the specific rotation of *l*-malic acid. Walden noticed that a similar but less marked effect is produced by uranium salts on *d*-tartaric acid, *d*-methyl tartrate, *l*-quinic, and *l*-mandelic acids, the increased rotation being in the same direction as the rotation of the aqueous solution of the substance. He concluded that the effect is limited to the active oxy-acids. As stated by Walden, the requisites of an agent which is to be used for the detection of malic acid by optical means are: (1) That the direction of rotation shall be constant, and (2) that the increase in rotation shall be as large as possible. This, of course, applies also to the quantitative estimation of malic acid. In addition, the agent in question should have little or no influence on any other substances which may occur in conjunction with malic acid. It has long been known that certain substances such as the oxygen compounds of boron,³ arsenic, antimony, molybdenum, and tungsten⁴ have the power of increasing the specific rotation of the oxy-acids. Uranium salts, however, are the only ones which fulfil the requirements just stated with any degree of satisfaction.

The authors have recently had the privilege of reading an article by P. A. Yoder, entitled "A Polariscopic

¹ Presented at the Indianapolis meeting of the American Chemical Society.

² *Ber. d. chem. Ges.*, [3] 30, 2889 (1897).

³ Biot, *Mém. de l'acad. roy. sci.*, 16, 229 (1838); *Ann. chim. phys.*, [3] 11, 82 (1884); 29, 341, 430 (1850); 59, 229 (1860). Pasteur, *Ann. chim. phys.*, [3] 59, 243 (1860).

⁴ Gernez, through Landolt's "Optical Rotation of Organic Substances," translated by Long, p. 248.

Method for the Determination of Malic Acid and its Application in Cane and Maple Products."¹ This paper was presented at the forty-second meeting of the American Chemical Society, in July, 1910, and contains the results of a large amount of work. The method outlined depends on the use of a uranium salt, but in other respects it differs materially from the one here proposed. With this exception, no one appears to have attempted the quantitative determination of malic acid by treatment with uranium.

THE METHOD IN BRIEF.

The method, in brief, consists in treating a portion of the neutralized solution² containing malic acid with uranyl acetate and polarizing it. The algebraic difference between the reading so obtained and that of the untreated solution is multiplied by the factor 0.036 to obtain the percentage of malic acid present. With the exception of *d*-tartaric acid, none of the common optically active substances interfere with the determination, and consequently they need not be removed. Uranyl acetate slightly decreases the rotation of sugars. This may give rise to an error in the estimation of small amounts of malic acid in the presence of large amounts of invert sugar. Hence, when the rotation of the original solution is negative and the approximate amount of sugar or malic acid is unknown, or when more than 10 per cent. of reducing sugars and less than 0.25 per cent. of malic acid are present, it is necessary to precipitate the malic acid and treat the filtrate with uranyl acetate also. In this case the polarization of this filtrate, instead of that of the untreated solution, is subtracted from the polarization of the solution containing both malic acid and uranyl acetate, and the difference is multiplied by 0.036.

DETAILS OF THE METHOD.

Dilute a measured volume of the solution, usually 10 cc., with quite a large volume of water, add phenolphthalein, and titrate with standard alkali to a decided pink color. Transfer another measured portion of the solution (75 cc. is a convenient volume) to a 100 cc. graduated flask, and add enough standard alkali, calculated from the above titration, to neutralize the acidity. A slight excess of alkali is not objectionable. If the solution is dark colored, add 5 or 10 cc. of alumina cream. Dilute to the mark, mix thoroughly, and filter if necessary through a folded filter.

(1) Treat about 25 cc. of the filtrate with powdered uranyl acetate, adding enough of the salt so that a small amount remains undissolved after two hours. Two and one-half grams of uranyl acetate will usually be sufficient, except in the presence of large amounts of malic acid. In case all the uranium salt dissolves more should be added. Allow the mixture to stand for two hours, shaking frequently. Filter through a folded filter until clear and polarize if possible in a 200 mm. tube. If the solution is too dark to read in a 200 mm. tube, a 100 or 50 mm. tube may be used.

¹ THIS JOURNAL, 3, 563 (1911).

² If no mineral acids are present it is not necessary to neutralize the malic acid.

It is desirable, however, to use the longest tube possible, in order to obtain the maximum rotation. This solution and reading will hereafter be designated as (1).

(2) Treat the remainder of the original filtrate with powdered normal lead acetate until no further precipitation results. Cool in an ice bath and filter through a folded filter until clear. Warm the filtrate to room temperature and add a small crystal of lead acetate to determine whether the precipitation is complete. If no further precipitate results, remove the excess of lead completely with anhydrous sodium sulphate, filter until clear, and polarize. Designate this filtrate as Solution (2) and its polarization as Reading (2). Care should be taken to add no more lead acetate to the solution than is necessary for complete precipitation, as lead malate is soluble in an excess of lead acetate. Solutions which are sufficiently clear and contain less than 10 per cent. of sugar may be polarized directly without treatment with lead acetate.

(3) If Reading (2) is negative treat a portion of Solution (2) with uranyl acetate in the manner described under (1) and polarize. Designate this as (3). If Reading (2) is positive, Reading (3) need not be made.

Polarize at room temperature with white light, taking care that all solutions are polarized at the same temperature. Make at least six readings in each case and take an average of these. In this work a standard, Lippich type, triple field saccharimeter was used, the light being furnished by an electric bulb placed behind a ground-glass plate. Calculate all readings to the basis of a 200 mm. tube. If Reading (3) is numerically less than Reading (2), the latter should be discarded; otherwise use Reading (2) in the subsequent calculation. Multiply the algebraic difference between this reading and Reading (1) by 0.036. The product will equal the percentage of malic acid

$$\left\{ \begin{array}{l} \text{CH}_2\text{COOH} \\ | \\ \text{CHOHCOOH} \end{array} \right\} \text{ in the solution as polarized.}$$

EFFECT OF URANIUM SALTS.

The method just described was developed in the course of some work on the composition of the apple. If uranium salts produce an increase in the rotation of malic acid only, it would theoretically be possible to estimate the amount of malic acid in a solution containing sugars and other organic compounds by simply polarizing the solution before and after the addition of the uranium salt and multiplying the difference in the readings by a factor determined experimentally. As was previously stated, the rotation of *d*-tartaric acid is also increased by uranium salts. Consequently, this method can not, without modification, be applied to a solution containing this acid. We have determined that, as would be expected, inactive lactic, succinic, and citric acids are unaffected by salts of uranium. There are, therefore, no serious difficulties in the way of applying this method to the determination of malic acid in the

absence of *d*-tartaric acid. Work is now in progress on the estimation of tartaric acid by a similar method.

In the earlier experiments of this investigation an attempt was made to use uranyl nitrate and potassium hydroxide as reagents, as recommended by Walden. This author states that a maximum rotation is obtained by the use of 4 molecules of potassium hydroxide and 1 to 4 molecules of uranyl nitrate $[\text{UO}_2(\text{NO}_3)_2 + 6\text{H}_2\text{O}]$ for each molecule of malic acid. He prefers the nitrate to the acetate because of the greater solubility of the former salt.

Uranyl nitrate, however, has one serious disadvantage. Its solution in water always contains nitric acid due to hydrolysis. It is impossible to obtain the maximum polarization in the presence of free mineral acid and it is therefore necessary, as Walden pointed out, to neutralize the solution when uranyl nitrate is used. The color of the solution always makes this operation very difficult. Many attempts were made to use uranyl nitrate, but with indifferent results. After addition of the uranyl nitrate solution to that containing malic acid, a solution of potassium hydroxide was added drop by drop until a precipitate just began to form. This was dissolved either by addition of a drop of nitric acid or of uranyl nitrate solution. The results, however, were very irregular. In some cases the theoretical recovery of malic acid was obtained, while in others the results were very much too low. Attempts to neutralize the solution, using various indicators, were made with similar results. No better success was attained when the amount of alkali required to neutralize both the uranyl nitrate and the malic acid solution was determined in advance and the calculated amount added to the mixture.

Uranyl acetate was then substituted for the nitrate in the hope that the presence of a weak organic acid like acetic acid would not influence the rotation of the uranium-malic complex. As a further precaution the solution to be examined was carefully neutralized before the addition of the uranium salt. The concentration of H ions in a solution containing acetic acid and sodium acetate is so slight that it was believed its influence on the rotation would be negligible. This procedure proved satisfactory and no further difficulty was experienced in this direction.

A number of experiments were made to determine what effect, if any, is produced by an excessive amount of uranyl acetate. The results all showed that such an excess does not influence the rotation of the solution. On the other hand, it is quite possible to add too small an amount of the salt to the solution under examination. In the case of solutions containing a comparatively large amount of malic acid, several hours may elapse before a maximum change in rotation is obtained. To test this point a solution containing 2.94 per cent. malic acid as sodium malate was treated with an excess of uranyl acetate, shaken frequently and polarized at intervals. The polarizations obtained were as follows:

	°V.
After 10 minutes.....	-60.4
35 minutes.....	-68.7
1 hour.....	-74.1
2 hours, 10 minutes.....	-82.0
2 hours, 45 minutes.....	-82.8
4 hours, 10 minutes.....	-83.0

This indicates that after two hours the reading is practically constant, since a difference of 1° corresponds to only 0.036 per cent. of malic acid. It must be remembered, however, that frequent agitation is also needed if a maximum is to be attained in this time.

An approximate determination of the solubility of uranyl acetate at ordinary temperatures gave the following results:

	Grams per 100 cc.
1. In water.....	8.5
2. In a solution containing 1.25 per cent. of malic acid as sodium malate.....	11.96
3. In a solution containing 2.5 per cent. of malic acid as sodium malate.....	13.32

REMOVAL OF THE MALIC ACID.

Walden reports $[\alpha]_D$ for a 0.65 per cent. solution of *l*-malic acid as approximately -0.77 circular degrees, as compared with -475° (circular) for the uranium complex. It is evident, therefore, that in ordinary concentrations the rotation of free malic acid is negligible. However, as has been said, it is sometimes necessary to remove the malic acid from the solution before making reading (2) for the reason that the addition of uranyl acetate causes a decrease in the rotation of strong sugar solutions.¹ To determine the extent of this effect, 13 grams of uranyl acetate were added to 100 cc. of various sugar solutions and allowed to stand one hour with frequent shaking. The solutions were then polarized in 200 mm. tubes with white light and the readings compared with those of the untreated solution. After standing over night the readings were repeated.

TABLE I.—EFFECT OF URANYL ACETATE ON THE ROTATION OF SUGARS.

Sugar.	Grams in 100 cc.	Sugar solution after 1 hour.		Sugar solution, after standing over night.	
		Without uranyl salt. °V.	After addition of uranyl salt. °V.	Without uranyl salt. °V.	After addition of uranyl salt. °V.
Cane sugar.....	26	+100.0	+97.5	+100.0	+97.3
Levulose.....	26	-125.4	-120.8	-126.0	-121.2
Dextrose.....	26	+82.4	+78.8	+80.4	+78.8
Invert sugar...	50	-61.9	-60.0
"	25	-28.6	-27.0
"	10	-10.9	-9.7

The results show a decided reduction in rotation which would have a serious effect on the determination of small amounts of malic acid in the presence of large amounts of sugar. To avoid inaccuracy from this cause it is necessary in some cases to remove the malic acid as completely as possible from solution (2) and then to add uranyl acetate to the filtrate. For reasons which will be given later this procedure is never followed when the rotation of solution (2) is

positive. Normal lead acetate is used to precipitate malic acid. Even when the removal of the malic acid is not necessary it is advisable to clarify the solution with lead acetate and then remove the excess of lead in order to obtain an easily readable solution. In the earlier work a solution of lead acetate was added to the malic acid solution before diluting to the mark. It was found, however, that the volume of the precipitate in some cases seriously changed the concentration of the solution, especially where sugar solutions inverted with hydrochloric acid were used, and the solid normal lead acetate, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$, was therefore substituted. This salt contains 4.7 per cent. of water of crystallization and introduces a negligible dilution error in the amounts used. An attempt was made to use Horne's dry lead subacetate, but the results were not satisfactory.

Dry neutral potassium oxalate was at first used to remove the excess of lead from the solution. It was later found that the rotation of sugar solutions is affected to some extent when this salt is added to an invert sugar solution containing lead acetate. An approximately 25 per cent. solution of invert sugar polarized -29° before and after addition of lead acetate. After precipitating the lead with potassium oxalate, however, the filtrate polarized -29.6° . Consequently anhydrous sodium sulphate was substituted for potassium oxalate with satisfactory results.

Lead malate is somewhat soluble in water, lead acetate, and sugar solutions. This fact has caused difficulty at two points during the development of the method. It was early discovered that when a solution of sodium malate is treated with lead acetate the filtrate has a positive polarization amounting to as much as one degree. Previous to this discovery it was not thought necessary to remove the lead from solution (2) before polarization. A more serious difficulty was encountered when it was found necessary to treat solution (2) with uranyl acetate. The presence of even a slight amount of malic acid in this solution after removal of the lead will of course cause a change in rotation when the uranium salt is added. To obtain the best possible separation of lead malate, therefore, the solution is cooled in an ice bath before filtering. This procedure is sufficient to remove most of the malic acid when quantities less than 0.2 per cent. are present, but if large amounts of the acid are present a very considerable error may be introduced by the change in rotation caused by the formation of the uranium-malic complex. This is illustrated by the following experiment:

Four solutions containing known amounts of malic acid, as sodium malate, were treated with lead acetate at room temperature, the lead removed with potassium oxalate, and the filtrate treated with uranyl acetate for one-half hour, with frequent shaking. The filtrates were polarized with the following results:

Per cent. of malic acid.	°V.
0.099	-0.1
0.199	-1.1
0.99	-3.2
1.99	-15.5

¹ Rembach and Weber (*Zischr. physik. Chem.*, **51**, 491 (1905)) have noticed that uranyl nitrate produces a slight increase in the specific rotation of solutions of dextrose and levulose containing 7.2 grams of the sugar in 100 cc. of solution.

When the solution, which has been treated with lead acetate, is cooled in ice water before filtering, the rotation with uranyl acetate is much decreased, so that if small amounts of malic acid occur in the presence of large amounts of invert sugar, Reading (3) is less than Reading (2). When comparatively large amounts of malic acid are present, however, Reading (3) is likely to be greater than (2), and for this reason both readings are made when the approximate amounts of invert sugar and malic acid are unknown, and the smaller is used in calculating the percentage of malic acid present.

In the presence of large amounts of sucrose the error due to the effect of the uranium salt on sugar is in the same direction as that due to the presence of traces of malic acid. This will be clearly seen from the following determinations on an approximately normal solution of sucrose containing 0.24 per cent. of malic acid.

TABLE II.—DETERMINATIONS ON A NORMAL SOLUTION OF SUCROSE CONTAINING 0.24 PER CENT. OF MALIC ACID.

Readings.	Polarization. °V.	Difference. °V.	Malic acid found. Per cent.	Recovery. Per cent.
1.....	+88.5
2.....	+95.6	7.1 ¹	0.26	108.3
3.....	+93.8	5.3 ²	0.19	79.2

It will be seen that when the difference between readings (1) and (2) is used in the calculations a somewhat high recovery is obtained. This is to be expected since the decrease in rotation due to the effect of the uranium salt on sugar is added to that due to the rotation of the uranium malic complex. Consequently, Reading (1) is lower, and the difference between (1) and (2) is higher, than it should be. Reading (3) is decreased by the combined effect of the action of the uranium salt on sugar and also on the traces of malic acid present. Hence, the difference between (1) and (3) is too small. The percentage recovery obtained by using the difference between readings (1) and (2) is not excessively high and this is the largest error that would be obtained, due to the action of uranium salts on sucrose, assuming that no more concentrated solution than one of normal sugar is examined. Therefore, while not theoretically correct, it is practically permissible to dispense with Reading (3) entirely when working with solutions in which Reading (2) is positive. It would, of course, be possible to avoid error from this source by inverting the solution before beginning the determination, then neutralizing, and diluting to a definite volume. This has not been found to be necessary in practice, however. When it is known that the solution under examination contains either less than 10 per cent. of invert sugar or more than 0.25 per cent. of malic acid it is unnecessary to make Reading (3).

Solutions are frequently encountered which are too dark to polarize without clarification. It was found that alumina cream can be used for this purpose without affecting the results.³

¹ Difference between (1) and (2).

² Difference between (1) and (3).

³ With very dark solutions such as fruit juices, C. W. Clark, of this laboratory, has found that a few drops of bromin may often be used to decolorize without affecting the results.

The question arises as to whether uranium salts produce the same effect on levo, dextro, and inactive malic acid. For ordinary work on natural products this question is of little importance, since, as far as the literature goes, malic acid appears to occur in nature only in the levo form. W. Gintl¹ reports the presence of the inactive form in the leaves of *Fraxinus excelsior* L., but this discovery does not appear to have been confirmed since that time.

It is well known that the specific rotation of aqueous solutions of *l*-malic acid varies greatly with concentration,² changing from minus to plus in the higher concentrations. The addition of concentrated sulphuric acid³ will also cause a change in rotation. Some experiments were made to throw light on the question as to whether such differences in the specific rotation of *l*-malic acid affect the rotation of the uranium malic complex. A solution containing 13.95 grams of *l*-malic acid in 28 cc. of solution polarized +1.1°. This solution was diluted and the malic acid determined by the uranium method, the theoretical recovery being obtained. This same solution was treated with concentrated sulphuric acid and after standing over night polarized +2.7°. After standing four days the rotation was found to be the same. On dilution the theoretical recovery was again obtained by the uranium method.

DETERMINATION OF THE FACTOR.

A large number of experiments were made to determine the factor for calculating the percentage of malic acid from the polarization. Neutral solutions containing known amounts of malic acid were treated with uranyl acetate, polarizing in a 200 mm. tube with white light and dividing the percentage of malic acid present by the reading in degrees Ventzke. In some cases this determination was made in the presence of invert sugar. The details of the experiment are given in Table IV, page 830. It will be observed that there is a gradual decrease in the factor with increase in concentration of malic acid. The increase is not sufficient, however, to seriously affect results in the ordinary concentrations found in natural products. The average of 27 determinations gave a factor 0.036, and this was accordingly adopted for use in all calculations. A number of determinations in which sodium light was used instead of white light showed a slightly smaller specific rotation with the former.

TABLE III.—SPECIFIC ROTATION IN CIRCULAR DEGREES (10 CM. TUBE).

Per cent. malic acid.	$[\alpha]_D$.	$[\alpha]_H$.
0.098	-442	-436
0.294	-457	-448
0.489	-470	-464
0.978	-476	-470
1.956	-495	-488

With very clear solutions containing large amounts of uranium-malic complex difficulty may be experienced in obtaining the neutral point on account of the decided blue color developed in one segment of the field. This can be eliminated to a great extent

¹ *Jahresber. Chem.*, 1868, p. 800.

² Schneider, *Ann. Chem. (Liebig)*, 207, 262 (1881).

³ *Ibid.*, p. 279.

by the use of a 3 cm. cell containing a 3 per cent. solution of potassium bichromate. The use of such a screen has the additional advantage of lowering the specific rotation of the uranium-malic complex somewhat and consequently partially correcting for the normal rise in specific rotation due to concentration.

TABLE IV.—DETERMINATION OF FACTOR.

Number of determination.	Invert sugar present (approximate). Per cent.	Malic acid present. Per cent.	Polarization.		Difference between readings (1) and (2).	Factor calculated.	Malic acid found, using factor 0.036. Per cent.	Recovery. Per cent.
			Solution 1—with uranium acetate. °V.	Solution 2—with-out uranium acetate. °V.				
1.....	2.48		-74.6		74.6	0.033	2.69	108.5
2.....	1.49		-43.5		43.5	0.034	1.57	105.4
3.....	2.5	1.49	-46.8	-3.0	43.8	0.034	1.58	106.0
4.....	0.99		-28.2		28.2	0.035	1.02	103.0
5.....	0.99		-28.5		28.5	0.035	1.03	104.0
6.....	2.5	0.99	-31.4	-2.9	28.5	0.035	1.03	104.0
7.....	5.0	0.99	-34.2	-5.9	28.3	0.035	1.02	103.0
8.....	0.99		-29.0		29.0	0.034	1.05	106.1
9.....	0.80		-22.8		22.8	0.035	0.82	102.5
10.....	0.60		-16.8		16.8	0.036	0.61	101.7
11.....	0.50		-14.2		14.2	0.035	0.51	102.0
12.....	0.50		-14.2		14.2	0.035	0.51	102.0
13.....	2.5	0.50	-17.0	-2.8	14.2	0.035	0.52	104.0
14.....	5.0	0.50	-19.8	-5.9	13.9	0.036	0.50	100.0
15.....	5.0	0.50	-19.7	-6.0	13.7	0.036	0.50	100.0
16.....	0.40		-11.3		11.3	0.035	0.41	102.5
17.....	0.30		-8.5		8.5	0.035	0.31	103.3
18.....	0.25		-7.0		7.0	0.036	0.25	100.0
19.....	2.5	0.25	-9.9	-2.9	7.0	0.036	0.25	100.0
20.....	5.0	0.25	-12.5	-5.8	6.7	0.037	0.24	96.0
21.....	0.20		-5.7		5.7	0.035	0.21	105.0
22.....	0.10		-2.8		2.8	0.036	0.10	100.0
23.....	2.5	0.10	-5.6	-2.8	2.8	0.036	0.10	100.0
24.....	5.0	0.10	-8.5	-5.8	2.7	0.035	0.10	100.0
25.....	0.050		-1.3		1.3	0.038	0.047	94.0
26.....	0.050		-1.3		1.3	0.038	0.047	94.0
27.....	2.5	0.050	-4.0	-2.75	1.25	0.040	0.045	90.0
Average factor. 0.036								

DISCUSSION OF RESULTS.

The results which have been obtained in the application of the method are tabulated in Tables V and VI, which are in the main self-explanatory. Table V contains the results of determinations in which known amounts of malic acid were added by the analyst, while the determinations recorded in Table VI were made on solutions in which the amount of malic acid was unknown. The percentages of invert sugar given in the second column of Table V are only approximate. This accounts for the fact that in some cases solutions containing the same amount of sugar and malic acid show a larger difference in polarization than can be accounted for by errors in reading. Stock solutions containing 5 or 10 per cent. of carefully weighed C. P. malic acid were made up and the percentages of acid present were determined by titration against standard alkali. A measured portion of the stock solution was then added to a definite volume of invert sugar solution and the mixture diluted to the desired concentration. The sugar solutions always contained more or less sodium chlorid resulting from the neutralization of the acid used for inversion. New malic acid stock solutions were made up every two or three days, as a

growth of mold usually appears after a few days' standing. In many cases Reading (3) was not made. Wherever possible it is given, however. It will be noted that in many cases Reading (3) is higher than (2) for the reason previously explained. When the former is lower, the percentage of malic acid is calculated from it. The most favorable concentrations of malic acid appear to be between 0.2 and 2.5 per

TABLE V.—DETERMINATIONS ON SOLUTIONS CONTAINING KNOWN AMOUNTS OF MALIC ACID.

Number of determination.	Invert sugar present (approximate). Per cent.	Malic acid present. Per cent.	Polarization.			Difference between readings. °V.	Malic acid found. Per cent.	Recovery. Per cent.
			Solution 1—with uranium acetate. °V.	Solution 2—with-out uranium acetate. °V.	Solution 3—with uranium acetate after removing malic acid. °V.			
1.....	10.0	2.98	-94.0	-11.9		82.1	2.96	99.3
2.....		2.49	-73.9			73.9	2.66	106.8
3.....	5.0	2.49	-77.6	-6.6		71.0	2.56	102.8
4.....	5.0	2.49	-75.0	-6.6		68.4	2.46	98.8
5 ¹	25.0	2.31	-93.2	-33.2	-36.5	60.0	2.16	93.5
6.....	25.0	1.99	-85.0	-29.0		56.0	2.02	101.5
7.....	25.0	1.99	-82.9	-32.9		50.0	1.80	90.5
8.....		0.99	-26.1			26.1	0.94	94.9
9.....	5.0	0.99	-32.1	-5.4		26.7	0.96	97.0
10.....	25.0	0.99	-59.2	-31.9		27.3	0.98	99.0
11.....	25.0	0.99	-54.9	-29.0		25.9	0.93	93.9
12.....	5.0	0.59	-22.7	-6.0		16.7	0.60	101.7
13.....		0.50	-12.7			12.7	0.46	92.0
14 ¹	5.0	0.49	-18.7	-5.9	-6.4	12.8	0.46	93.9
15 ¹	10.0	0.49	-26.6	-12.3	-13.0	14.3	0.51	104.1
16 ¹	15.0	0.49	-31.0	-17.8	-18.6	13.2	0.48	98.0
17 ¹	25.0	0.49	-45.1	-31.4	-32.1	13.7	0.49	100.0
18.....	5.0	0.39	-16.9	-6.0		10.9	0.39	100.0
19.....	2.5	0.35	-12.3	-2.7		9.6	0.35	100.0
20 ¹	5.0	0.25	-12.5	-6.0	-6.2	6.5	0.24	96.0
21 ¹	10.0	0.25	-18.7	-12.0	-12.2	6.7	0.24	96.0
22 ¹	15.0	0.25	-23.8	-17.2	-17.4	6.6	0.24	96.0
23 ¹	25.0	0.25	-37.8	-31.6	-31.9	6.2	0.22	88.0
24.....	2.5	0.20	-8.1	-2.7		5.4	0.19	95.0
25.....	5.0	0.20	-11.6	-6.0		5.6	0.20	100.0
26.....		0.20	-5.2			5.2	0.19	95.0
27.....	12.5	0.20	-18.7	-14.2	-13.7	5.0	0.18	90.0
28.....	25.0	0.20	-34.5	-30.0	-29.1	5.4	0.19	95.0
29.....	25.0	0.20	-33.3	-29.5	-28.3	5.0	0.18	90.0
30.....	5.0	0.19	-10.1	-5.1		5.0	0.18	94.7
31.....	2.5	0.099	-5.2	-2.6		2.6	0.094	94.9
32.....	5.0	0.098	-8.6	-6.0	-6.0	2.5	0.094	95.9
33.....	2.5	0.050	-3.8	-2.6		1.2	0.043	86.0

TABLE VI.—MALIC ACID DETERMINATIONS ON UNKNOWN SOLUTIONS.

Number of determination.	Solvent.	Malic acid present. Per cent.	Polarizations.			Difference between readings.	Malic acid found. Per cent.	Recovery. Per cent.
			Solution 1—with uranium acetate. °V.	Solution 2—with-out uranium acetate. °V.	Solution 3—with uranium acetate after removing malic acid. °V.			
1. Bottled strawberry juice.....		0.25	-8.1	-2.5		5.6	0.27	108.0
2. Bottled strawberry juice.....		0.90	-22.6	-3.8		18.8	0.90	100.0
3. Bottled strawberry juice.....		0.25	-8.2	-4.3		3.9	0.19	76.0
4. Fresh strawberry juice.....		0.50	-12.4	-2.6		9.8	0.47	94.0
5 ¹ Fresh strawberry juice.....		0.50	-12.0	-1.8	-2.2	10.2	0.49	98.0
6 ¹ Fresh strawberry juice.....		0.37	-10.0	-2.6	-2.4	7.6	0.37	100.0
7 ¹ Fresh strawberry juice.....		0.62	-13.6	-2.1	-3.0	11.5	0.55	88.7

¹ Determinations by C. W. Clark.

cent. Below 0.2 per cent. the increase in polarization due to the uranium-malic complex is so small that a small error in reading may make a relatively large error in the final result, while above 2.5 per cent. the increase in specific rotation tends to give high recoveries.

The results shown in Table VI illustrate the applicability of the method to natural products. The strawberry juice used as a solvent was highly colored and most of the readings had to be made in 50 or 100 mm. polariscope tubes.

SUMMARY.

(1) When a neutralized solution of malic acid is treated with uranyl acetate, its rotation is increased approximately 28° V. for each per cent. of malic acid in the solution; *d*-tartaric acid is the only other common acid which is affected in this way by uranyl acetate. Hence, in the absence of *d*-tartaric acid, malic acid may be determined quantitatively by treating its solution with uranyl acetate, polarizing, and multiplying the difference between this reading and that of the untreated solution by 0.036. The product equals the percentage of malic acid present.

(2) In the presence of more than 10 per cent. of reducing sugars and less than 0.25 per cent. of malic acid, the results may be affected by the action of uranyl acetate on the rotation of the sugar. Hence, in this case or when the amounts of sugar or malic acid are unknown, certain simple modifications are necessary.

(3) For this determination, the most favorable limits of concentration of malic acid are between 0.2 to 2.5 per cent. The percentage error seldom amounts to more than 5 per cent. of the malic acid present. Twelve complete determinations may easily be made in four hours time, including two hours during which the solutions require no treatment other than frequent shaking.

BUREAU OF CHEMISTRY,
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THE EFFECT OF PHOSPHORUS MANURING ON THE AMOUNT OF INORGANIC PHOSPHORUS IN FLAT TURNIP ROOTS.

By BURT L. HARTWELL AND FREDERICK S. HAMMETT.

Received June 21, 1911.

It has been stated¹ that the percentage of total phosphorus in turnips is influenced by the amount of available phosphorus in the soil. Advantage has been taken of this fact in ascertaining the relative deficiency of available phosphorus in soils. It appears as a result of further study as if the inorganic phosphorus is influenced even more than the total; if this is so its determination would prove more useful for this purpose than that of the total phosphorus. Microchemical examinations for inorganic phosphorus in sections of fresh turnips were made with a mixture of magnesium sulphate and ammonium chloride;² only such an amount of ammonium hydroxide was used as was absolutely necessary, for fear that inorganic phosphorus would be developed from any phosphoproteins which might be present.

Part of the material used for examination was from coöperative experiments with flat turnips, carried on in different parts of the State to secure data concerning the availability of the phosphorus in the soils. All of the plats which will be considered in this connection were well supplied with lime, nitrogen and potassium. In each experiment, one plat did not receive any application of phosphate; a second received a liberal amount of acid phosphate; and a third received still more, in order to show whether the second had been supplied with enough to produce a maximum crop.

As a result of the microchemical examination of small young turnips from five different localities, no crystals of ammonium magnesium phosphate were observed either in the turnips from the no-phosphate plats, or in those receiving the smaller application of phosphate, with the exception of a few crystals in the case of turnips from a single soil naturally well supplied with phosphorus. Where the larger applications of phosphorus were made, crystals were found, but small turnips as a rule appeared to contain only a small amount of inorganic phosphorus according to this test. Fresh turnips of a similar small size when examined later in the season, however, generally yielded a few crystals and those from the single soil referred to above contained considerably more than when previously examined.

Early in the season the *larger* turnips from the no-phosphate plats, on the contrary, yielded, generally, some crystals, although in case of certain of the soils, which were very deficient in phosphorus, scarcely any were found. Large turnips from the plats to which acid phosphate had been added invariably yielded crystals, and in some cases they were very abundant.

As a result of a single season's observations, indications are afforded that the relative abundance of crystals formed by adding the magnesium-ammonium salt solution to sections of the larger turnips grown on different soils is correlated, to a certain extent at least, with the relative amount of available phosphorus at the disposal of the plant.

Considerable quantitative chemical work was done on turnips from two of the station plats in which the amount of available phosphorus was quite different as indicated by the fact that the plat to which a liberal application of acid phosphate was made yielded thereby nearly twice as much as the other.

The microchemical tests made on different dates revealed no crystals in turnips from the plat which was very deficient in phosphorus, even when the larger turnips were examined, except a few at the end of the season; whereas the crystals were always plentiful in turnips from the phosphate plat.

Although differences in the ratio of inorganic to total phosphorus were found by precipitating the inorganic phosphorus by magnesium, as well as by the molybdenum, mixture, the results did not confirm the microchemical findings, in that considerable phosphorus was precipitated by these mixtures from turnips which yielded no crystals. It was feared, there-

¹ Hartwell and Quantz. *Jour. Biol. Chem.*, 7, XXXVIII (1910).

² Zimmermann, "Botanical Microtechnique," 53 (1901).

fore, that these particular reagents precipitated a larger amount of inorganic phosphorus than existed originally, especially in case of turnips grown on the soil deficient in phosphorus. Their use was finally abandoned and the inorganic phosphorus determined in accordance with the following directions: grate portions of fresh turnips in the presence of sufficient acetic acid to equal about 2 per cent. of the moisture, finally squeeze the juice from the pulp, filter, add to an aliquot, barium chlorid solution with constant stirring, then carefully neutralize with ammonium hydroxid, allow to stand about a day, filter, wash, dissolve as much as possible of the contents of the filter in hot water and dilute nitric acid, wash, and determine the phosphorus in the filtrate, by molybdenum and magnesium mixtures in the usual way. In calculating the percentage of inorganic phosphorus in the turnips it was assumed that the percentage of phosphorus in the expressed juice was the same as that in the moisture remaining with the pulp. A determination of moisture in the turnips, therefore, made it possible for the results to be calculated on the basis of dry turnips.

The above method was adopted after the following observations had been made regarding the amount of inorganic phosphorus, namely: that it increased upon heating the natural juice; that it increased when the natural unheated juice was allowed to stand; that it did not increase on standing subsequently to the addition of acetic acid; that it increased if an excess of ammonium hydroxid was added at the time of precipitation with barium chlorid; that it was fully recovered along with that in a standard solution of sodium phosphate added to the juice; and that it was not increased by digesting the pulp with dilute hydrochloric acid, but that this digestion rendered its determination difficult on account of the presence of pectin-like compounds.

The uncertainties as to just what constitutes so-called inorganic phosphorus in work of this kind are fully recognized, and it is intended, as soon as material is available, to subject the method to further tests regarding its accuracy. All things considered, however, it is not believed that the differences which are shown in the following table are exaggerated.

PER CENT. OF PHOSPHORUS PENTOXID CALCULATED TO THE DRY MATTER OF TURNIP ROOTS.

	Total in turnips.		Total in juice, pulp grated in presence of acetic acid.		Inorganic, determined in the same juice.		Ratio of P_2O_5 in No-P. plat to that in P. plat, per cent.	
	No-P. plat.	P. plat.	No-P. plat.	P. plat.	No-P. plat.	P. plat.	Total.	Inorganic.
Oct. 17th, small turnips.	0.50	0.85	0.22	0.61	0.02	0.13	58	15
Nov. 1st, small turnips.	0.50	0.84	0.23	0.53	0.03	0.24	60	13
Nov. 1st, large turnips.	0.44	0.84	0.31	0.52	0.06	0.26	52	24

It may be seen by reference to the last two columns of the above table that although the content of total

phosphorus in turnips was nearly doubled by the addition of a liberal amount of acid phosphate, the content of inorganic phosphorus was increased about six-fold.

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TIN SALTS IN CANNED FOODS OF LOW ACID CONTENT, WITH SPECIAL REFERENCE TO CANNED SHRIMP.

By W. D. BIGELOW AND R. F. BACON.

Received September 28, 1911.

INTRODUCTION.

It is customary to attribute the presence of tin salts in canned foods to the action of the acids of those foods upon the tin of the container. We usually think of the action of a food upon the tin as proportional to the acidity of the food.

The acidity of many products ordinarily preserved in cans is so high and their effect on the tin lining of the container so marked as to offer a sufficient explanation of the amount of tin salts they contain, and until recently the high tin content of certain vegetables and other products of low acidity was overlooked or regarded as accidental. The interest lately awakened in the subject of tin salts has led to a more careful study of the question than has been given it before and it is now recognized that several articles such as certain varieties of fish, beets, lima beans, asparagus, and pumpkin, though being almost without acidity, have a marked solvent action upon the tin lining of the container in which they are preserved. As far as we are aware, however, no explanation of this fact has been offered.

TIN CONTENT OF CANNED GOODS VARYING IN ACIDITY AND AGE.

The relation of the acid to the tin content of a series of canned goods, examined about six months after they were packed, is well shown by the following table in which the acidity is expressed as acetic acid and the amount of tin is stated in milligrams per kilogram of the canned food and as milligrams of tin for each 100 mg. of acid. In the table those foods having the highest amount of tin in relation to their acidity are given first, and it is seen that the fruits whose action on tin is most familiar to us because of their high acidity come last in the list with from 1 to less than 5 mg. of tin per 100 mg. of acid.

In some of the vegetables considered in this table the ratio of tin to acid is a little higher than in the case of some of the fruits shown. It is distinctly higher in all cases, however, especially if the pears, which are somewhat anomalous in one other respect, are excluded. Moreover, in the fish and in a number of the vegetables the ratio of tin to acid is strikingly higher than in the fruit. In a general way the ratio of tin to acid in the fruits appears to depend on the variety of the acid the fruit contains, the solvent action of citric acid, to which the acidity of raspberries and tomatoes is due, being less than that of malic acid. Pears appear to be an exception to this rule, however, since, notwithstanding the fact that

their characteristic acid is malic, they contain a greater amount of tin in proportion to their acidity than any of the other fruits.

TABLE 1.—ACIDITY AND TIN CONTENT OF CANNED GOODS ABOUT SIX MONTHS AFTER PACKING.

Substance.	Acidity as acetic acid. Per cent.	Milli- grams of tin per kilogram.	Milligrams tin per 100 milligrams of acid.
Salt fish.....	0.012	90	75.0
Salt fish.....	0.012	112	93.3
Beets.....	0.036	262	72.8
Corn.....	0.012	33	27.5
Corn.....	0.012	46	38.3
Pumpkin.....	0.072	193	26.8
Lima beans.....	0.017	36	21.2
String beans.....	0.108	80	7.4
String beans.....	0.108	98	9.1
Pumpkin.....	0.156	117	7.5
Pumpkin.....	0.156	93	6.0
Corn.....	0.019	12	6.3
Peas.....	0.126	69	5.5
Peas.....	0.126	57	4.5
Peas.....	0.025	13	5.2
Pears.....	0.180	86	4.8
Pears.....	0.180	79	4.4
Raspberries.....	0.450	174	3.9
Tomatoes.....	0.390	290	7.4
Tomatoes.....	0.390	145	3.7
Tomatoes.....	0.234	84	3.6
Cranberries.....	0.534	180	3.3
Cherries.....	0.966	146	1.5
Peaches.....	0.486	90	1.9
Grapes.....	0.510	61	1.2
Plums.....	0.582	63	1.1

It is obvious that in data of this kind conclusions must be drawn from the data as a whole rather than from the analyses of individual cans. For instance, one of the samples of tomatoes has 7.4 mg. of tin for each 100 mg. of acid, whereas the second sample, put up at the same time and from exactly the same batch of tomatoes, but in a different kind of plate, contains but 3.7 mg. of tin for each 100 mg. of acid. A wide difference is shown also among the samples of corn and of pumpkins examined. The general trend of the results is so striking, however, as to indicate that individual differences may be overlooked for the present and can not be regarded as overthrowing the generalization that the products given first in Table 1 contain some substance other than acid that has a marked solvent action on tin.

TABLE 2.—ACIDITY AND TIN CONTENT OF OLD CANNED GOODS.

Substances.	Average age of sample in years.	Acidity as per cent. acetic acid.	Milli- grams tin per kilogram.	Milligrams tin per 100 milligrams acid.
Yellow beets.....	Over 3	0.05 ^a	725	145
String beans.....	Over 10	0.04	551	138
Corn.....	10	0.11	563	51
Succotash.....	Over 3	0.10	444	44
Mock turtle soup.....	Over 5	0.10	306	30
Asparagus.....	2 to 3	0.13	333	26
Tomatoes.....	16	0.48	944	20
Peaches.....	Over 3	0.43	786	19
Apples.....	Over 5	0.22	364	17
Red kidney beans.....	Over 10	0.23	313	14
Blackberry jam.....	8	0.31	383	12
Roast beef.....	Over 10	0.33	426	11
Beans (baked).....	18	0.34	388	11
Apricots.....	Over 3	0.49	487	10
Lima beans.....	8	0.19	170	9
Green gages.....	Over 3	0.69	519	8
Apple butter.....	Over 5	1.05	690	7

Table 2 gives the results obtained in the examination of a series of samples of unknown origin, but

whose age is known to be at least as great as that stated. In general the results given therein are similar to those shown in Table 1.

STUDY OF CANNED SHRIMPS.

It is evident from these tables that in a study of the tin salts present in canned foods there is some important factor besides their acidity. It was thought that some light might be thrown upon this subject by the study of canned shrimps. It is recognized by packers that shrimps contain some corrosive substance which greatly interferes with their handling and preservation. It attacks the workmen's hands, causing the skin to peel, and also eats through the leather of their shoes. Tins in which the shrimps are preserved are quickly perforated. Packers have found that this substance seems to disappear when the shrimps are preserved with ice. Ordinarily they are caught at some distance from the packing houses and iced in the boats, so that by the time they reach the packer their corrosive property has disappeared to such an extent as to make it practicable to work with them. When caught near the packing house it is now customary to lay them down with ice for a day or so, during which time they lose this corrosive property.

There were recently received at this laboratory from A. W. Bitting several cans of headless shrimps—that is, shrimps from which the heads have been removed but not the shells—procured by him and packed in his presence at Biloxi, Miss. It was found that they contained a volatile alkaline substance, apparently monomethylamin, which attacks tin quite markedly and which also attacks the skin of the hands. From the volatile nature of the alkali it seems possible that the portion of it on the surface of the shrimp may escape when the shrimps are preserved on ice for a time and so explain the fact that shrimps so treated do not attack the skin. Even when so treated, however, special precautions must be taken to protect cans in which shrimps are preserved. Ordinary tin containers employed for the preservation of shrimps are rapidly corroded and the lining completely removed. To prevent this the cans are lined with parchment paper and corrosion is then only noted at the junction of the papers and at points where for some reason the paper is pressed against the tin coating. As the points of junction of the paper leave a free opening the reason for the attack there is self-evident. The attack at places where the paper is pressed against the can is believed to be due to surface action. The liquor separated from the shrimps was found to be alkaline to litmus. The alkalinity was measured as follows:

50 grams of this liquor required 8.1 cc of tenth-normal hydrochloric acid to make it neutral to azolitmin:

50 grams of this liquor required 44.5 cc of tenth-normal hydrochloric acid to make it neutral to methyl orange:

50 grams of this liquor required 15 cc of tenth-normal sodium hydroxid to make it neutral to phenolphthalein.

These results show that this liquor contains quite a large quantity of a moderately weak base partly combined with a weak acid, and hence largely hydrolyzed to contain considerable numbers of hydroxyl ions.

Some shrimps were extracted with alcohol and the volatile alkali distilled over as given below. This alkali was just neutralized with hydrochloric acid and the resulting solution evaporated to dryness on a steam bath. In the white, crystalline, deliquescent salt so obtained chlorine and nitrogen were determined with the following results:

TABLE 3.—ANALYSIS OF THE VOLATILE ALKALI.

Determinations.	Found.	Calculated for $N(CH_3)_2H_2Cl$.
Chlorine.....	52.0	52.5
Nitrogen.....	21.4	20.9

The chlorplatinate of this amin was found to consist of bright yellow crystals containing 41.9 per cent. of platinum. The theoretical amount in

$(N(CH_3)_2H_2)_2PtCl_6$ is 41.3 per cent.

Twenty cans of shrimps were ground up, covered with alcohol, and allowed to extract for two days. The extract was passed through muslin and the filtrate made slightly acid with sulphuric acid and evaporated to a small volume. To this extract magnesium oxid was added in excess and the volatile alkali distilled. The distillate, which smelled much like ammonia, was just neutralized with sulphuric acid and alcohol was added, causing the separation of a crystalline precipitate.

This was dissolved in water and reprecipitated with alcohol, giving 6 grams of dry salt. Some of this salt was distilled with sodium hydrate, the distillate (marked Solution I) made up to such a volume that it was a decinormal alkali, and its solvent action on tin was determined. When this solution was boiled for one hour with two plates of thin block tin, each 2 by 3 inches, 6 mg. went into solution from each plate. Another portion of the solution, after neutralization with hydrochloric acid, was boiled in the same manner and dissolved 5.8 mg. from each plate. A tenth-normal solution of methylamin treated in the same manner dissolved 5.7 mg. of tin from each place. Similar plates were boiled for one hour in dilute solutions of other alkalis, amins, and amino acids, including one of the purin bases, with the following results:

	Mg. per plate.
Sodium hydroxid, tenth-normal.....	5.0
Potassium hydroxid, tenth-normal.....	7.5
Ammonium hydroxid, tenth-normal.....	1.3
Sodium hydroxid, fourth-normal.....	6.2
Acetamid, 2 per cent.....	6.5
Asparagin, 3 per cent.....	4.4
Asparagin, 0.3 per cent.....	4.3
Aspartic acid, 0.3 per cent.....	3.7
Alanin, 0.3 per cent.....	2.4
Glycocoll, 0.3 per cent.....	3.3
Sarkosin, 0.3 per cent.....	5.0
Tyrosin, 0.3 per cent.....	2.4
Hypoxanthin, 0.3 per cent.....	4.2
Creatin, 0.3 per cent.....	2.9
Leucin, 0.3 per cent.....	1.7

DETERMINATION OF VOLATILE BASES IN OTHER COMPARATIVELY NON-ACID FOODS.

It appears, therefore, that monomethylamin exists to a considerable extent in shrimps, and explains

largely their corrosive action on tin containers. The thought suggests itself that the solvent action of certain other non-acid or slightly acid foods may be explained in the same manner, and that amins and amino acids as a class may have a marked solvent effect on tin. These bodies are known to be present in practically all fish. According to Schreiber,¹ beets contain 0.25 per cent. of betain and ripe beets 0.10 per cent. Asparagin has been found in asparagus, several vetches, beets, beans, and sometimes in peas. Although asparagin is formed especially during the germination of these products, it is also present in the unripe vegetables. Among the vegetables which are recognized as strongly attacking tin containers are asparagus, spinach, string beans, and pumpkin. Samples of these substances of unknown history were procured and the acidity to phenolphthalein, the measure of amino acid by titration after adding formaldehyde (Sorensen's method), alkalinity to methyl orange, and total volatile alkali were determined in each case. The results are given in the following tabular statement calculated for 100 grams of sample. It is suggested that these volatile alkalis and amino acids are responsible to a great degree, if not entirely, for the solvent action on tin exerted by foods of very low acidity.

VOLATILE BASES IN CANNED GOODS.

Determination.	Asparagus (can badly corroded).	Spinach (can badly cor- roded).	String beans (can but little cor- roded).	Pumpkin (can badly corroded).
(1) Titration to phenolphthalein (cc. $N/10$ NaOH).....	20.0	20.0	12.0	20.0
(2) Same as (1). Calculated as per cent. of acetic acid....	0.12	0.12	0.07	0.12
(3) Titration after adding 10 cc. formaldehyde to the neu- tral solution (cc. $N/10$ NaOH) ²	32.0	23.0	29.0	24.0
(4) Same as (3). Calculated as per cent. of aspartic acid....	0.43	0.31	0.38	0.32
(5) Titration to methyl orange (cc. $N/10$ HCl).....	13.0	29.0	13.0	28.0
(6) Volatile alkali, titration to methyl orange (cc. $N/10$ HCl).....	9.7	6.7	4.0	7.7

It is evident that the volatile alkalis and amino acids which occur in these vegetables probably have an effect on the tin container analogous to that of the methylamin found in shrimp. Further work on this subject is in progress but, considering the number of chemists who are studying the content of tin salts in canned goods, it seemed best to offer this preliminary statement for the purpose of bringing to the attention of other workers certain phases of tin corrosion which seem to be of considerable importance and which have not been recognized heretofore. Acknowledgment is made to F. W. Liepsner and C. W. Clark for much of the analytical work done in connection with the investigation.

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¹ *Ber. d. chem. Ges.*, **3**, 155 (1870).

² Corrected for the acidity of formaldehyde.

THE USE OF SPICES AS PRESERVATIVES.

BY CONRAD HOFFMANN AND ALICE C. EVANS.

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During recent years there has been a good deal of discussion and legislation on food preservatives. Sodium benzoate has been of particular interest because some experts maintain that it is not harmful to the human system when used in quantities that will prevent the growth of microorganisms in food, whereas others ascribe injurious properties to it, and strongly condemn its use. However, much of it has been used, especially where an inferior grade of material is utilized and as yet there is no law preventing its use. As a result of this controversy over sodium benzoate, the public has become suspicious of it, and most people would prefer not to eat food containing it. At this time, therefore, it is interesting to consider the preserving properties of various articles which we commonly use in our food.

It is a matter of common knowledge that fruits or vegetables prepared with the addition of spices and vinegar keep longer without being carefully sealed than do those same fruits or vegetables put up alone or with only ordinary amounts of sugar. Unsealed pickles and ketchups will keep for a long time without the growth of microorganisms. Cakes containing spices are also known to keep longer than other cakes. Fruit cake, which always contains spices, is often made several weeks before using, since its quality is said to improve with age. Although it is known in a general way that spices have something to do with the keeping of food to which they have been added, yet they have never been used with the idea of exerting a preservative effect. The spices are added on account of the flavor which they impart, and it is only a lucky coincidence that they also help to keep the food from spoiling.

When spices are used in food, several kinds are almost always added together, and usually the cooking is done in a liquid which contains more or less vinegar. It is common to add to pickles and ketchups, especially, as many as six or eight kinds of spices. Just which of them have any value in preserving the food is not generally known.

All condiments are irritating to the mucous membrane and are injurious when used in excessive

amounts. As will be seen in the tables below, some of the most irritating spices have no value whatever as preservatives.

Vinegar in sufficiently high concentration prevents the growth of microorganisms, and must be considered an important preservative. A single test was made with vinegar: 100 cc. of vinegar were added to 100 grams of apple sauce (about 1 part water to 8 parts of apples by volume), the mixture was boiled over a flame until the volume was again reduced to 100 cc., it was exposed to the air for a few days and then stoppered to prevent evaporation. The sauce has not spoiled after 4½ months. Although a single experiment was performed, it seems to indicate that the vinegar exerts a preservative action. In much less concentration the vinegar would no doubt retard growth. The vinegar employed in this operation contained about 25% acetic acid.

A few experiments were carried out under conditions that would obtain in any kitchen to compare the preserving properties of various spices, and to determine the amounts of them which will prevent all growth of microorganisms. Apple sauce to which a small amount of sugar had been added was used in all of the tests except those on ginger, black pepper, and cayenne pepper recorded in Table I, where cabbage was used. In every case the given amount of spice was mixed with 100 grams of the cooked material in small Erlenmeyer flasks. After adding the spice the flasks were placed in the steam sterilizer and steamed for 30 minutes. When removed from the sterilizer they were left open in the laboratory for a few days to receive contamination from the air and then closed with cork stoppers to prevent evaporation. The figures in the tables show the number of days after being put up when a change was first observed in the flasks. It was assumed that the growth of yeasts, molds, or bacteria would change the appearance or odor of the sauce, and no further tests for growths were made. In every case it was the molds which first made their appearance. The flasks in Table I were not examined between the 60th and 100th days, so that the exact time of the spoilage of the apple sauce containing allspice in 3 of the flasks is not known. The tests recorded in Table I were preliminary, and the results served to suggest the amounts of spices to be used in later experiments.

TABLE I.—TIME OF SPOILAGE OF FOOD CONTAINING VARYING AMOUNTS OF GROUND SPICES.

Amount of spice. Grams.	Control.	Nutmeg.	Cinnamon.	Allspice.	Cloves.	Ginger.	Black pepper.	Cayenne pepper.	Mustard.
0	4 days
2.5	...	5 days	...	16 days	...	5 days	4 days	4 days	...
5.05	...	6 days	5 days	4 days	4 days	...
7.5	...	7 days	Not spoiled in 14 months	Between 60 and 100 days	Not spoiled in 14 months	5 days	4 days	4 days	Not spoiled in 14 months
10.0	...	16 days	5 days	4 days	4 days	...
15.0	...	27 days	...	195 days	...	5 days	4 days	4 days	...

amounts. Their use, then, must be limited. Hence every housewife should know just which of the condiments she adds in her cooking will help to preserve the food, and which of them are of no value except for their flavor, so that she can regulate her use of them

From Table I it appears that ginger, black pepper and cayenne pepper do not prevent the growth of microorganisms, but that cinnamon, cloves, and mustard are valuable preservatives and nutmeg and allspice delay growth. Further experiments were carried out

to determine more accurately the amounts that will prevent growth.

Flasks were again put up with ginger, black pepper, and cayenne pepper in large amounts. The results are given in Table II. Even where the large amounts of 30 grams of spice to 100 grams of apple sauce were used growth took place only two or three days later than in the control flask. Bitting¹ reports that molds will grow in a few days on a paste made of these ground spices mixed with water. It is obvious, then, that ginger, black pepper, and cayenne pepper can be of no value as preservatives in the small proportions they are used in cooking.

TABLE II.—TIME OF SPOILAGE OF APPLE SAUCE CONTAINING VARYING AMOUNTS OF SPICE.

Amount of spice. Grams.	Control.	Ginger.	Black pepper.	Cayenne pepper.
0	4 days
15	...	6 days	...	7 days
20	...	8 days	6 days	7 days
30	...	7 days	6 days	6 days

The effect of cinnamon, cloves, mustard, allspice, and nutmeg in small amounts was tested in another experiment. The results are given in Table III.

TABLE III.—TIME OF SPOILAGE OF APPLE SAUCE PRESERVED WITH SPICES.

Amount of spice. Grams.	Control.	Cinnamon.	Cloves.	Mustard.	Allspice.	Nutmeg.
0	9 days
0.25		9 days	15 days	115 days	9 days	
0.50		30 days	15 days	60 days	9 days	
1.00		84 days	74 days			9 days
1.50		84 days	{ Not spoiled in 8 months			
2.00		{ Not spoiled in 8 months		{ Not spoiled in 8 months	9 days 16 days 9 days	
2.50						9 days
5.00						9 days
7.50						9 days
10.00						10 days

Allspice in the proportion of 5 grams of spice to 100 grams of sauce did not have even a retarding effect, although the flask containing 2.5 grams kept 16 days, whereas the control flask kept 9 days. Nutmeg in the proportion of 10 grams to 100 grams of sauce delayed growth only 1 day. Hence these two spices cannot be considered of practical value as antiseptics.

Cinnamon, cloves, and mustard are about equal in their efficiency. The flask containing 0.5 gram of mustard kept for almost four months; the flask containing 1 gram kept two months; and the flasks containing 2, 2.5, and 5 grams are still keeping, eight months after having been put up. The flask containing 0.5 gram of cinnamon kept one month; the flasks containing 1 and 1.5 grams kept almost three months; and the flask containing 2 grams is still keeping. Cloves in the proportion of 0.25 gram to 100 grams of sauce delayed growth for several days; the flask containing 1 gram kept for 2½ months; and the flasks containing 1.5 and 2 grams are still keeping.

The three spices, cinnamon, mustard and cloves, must be considered important preservatives. Cinnamon and mustard are particularly valuable, for they are palatable even when used in proportions that

prevent all growth. Cloves in the proportion which prevented growth (1.5 grams to 100 grams of sauce) had too much of a burning taste to be palatable. However, it retards growth in much smaller amounts.

The active antiseptic constituents of mustard, cinnamon, and cloves are their aromatic or *essential* oils, as they are termed. Clove buds yield about 15 per cent of essential oils, of which the greatest part is eugenol, or oil of cloves. Cinnamon bark yields from 0.5–1 per cent of essential oils. About 70 per cent of this is cinnamic aldehyde, which gives to cinnamon its characteristic odor. The essential oil of cinnamon also contains from 4–8 per cent of eugenol and some other aromatic compounds in smaller amounts.

The much smaller yield of the essential oil from cinnamon bark as compared with that from clove buds is compensated by its much greater antiseptic properties, which are brought out in Tables IV and V. These tests also were made with apple sauce.

Cinnamic aldehyde even in the smallest proportion used—a little over 1/100 of a gram to 100 grams of sauce—delayed growth 60 days, and in double this amount prevented growth entirely in the second

set of flasks. As in the case of the cinnamon from which it is derived, cinnamic aldehyde is palatable in proportions which will preserve food.

TABLE IV.—TIME OF SPOILAGE OF APPLE SAUCE PRESERVED WITH ESSENTIAL OILS.

Amount of oil. Gram.	Control.	Cinnamic aldehyde.	Eugenol.
0	3 days
0.026	...	80 days	6 days
0.052	...	120 days	12 days
0.105	...	{ Not spoiled in 14 months	{ Not spoiled in 14 months
0.157	...		
0.21	...		

TABLE V.—TIME OF SPOILAGE OF APPLE SAUCE PRESERVED WITH ESSENTIAL OILS.

Amount of oil. Gram.	Control.	Cinnamic aldehyde.	Eugenol.
0	9 days
0.013	...	60 days	9 days
0.026	...	{ Not spoiled in 8 months	13 days
0.052	...		9 days
0.105	...		Not spoiled in 8 months

It required considerably higher proportions of eugenol for complete preservation. In both tests, 0.105 gram of eugenol to 100 grams of sauce prevented all growth. This amount gives too much of a

¹ "Experiments on the Spoilage of Tomato Ketchup," by A. W. Bitting, Bureau of Chemistry, *Bull.* 119, U. S. Dept. of Agriculture.

burning taste to be palatable, which is in agreement with the results obtained with cloves. One-half of this amount delayed growth somewhat, and did not give too strong a flavor. The essential oils of both cinnamon and cloves, however, lack much of the good flavor of the spices.

In continuation of the above work, it was thought advisable, in view of the present controversy relative to the manufacture of ketchups and the use of preservatives therein, to examine various ketchups as to the types of organisms present. Spices are extensively used in the manufacture of ketchup and in many commercial brands sodium benzoate is employed as a preservative. The use of sugar also has been adopted as aiding the keeping qualities of ketchups.

Accordingly any organisms which could grow in such a medium would be more or less of a resistant type and upon such a critical and crucial test of the preservative action of various substances could be made. In previous work these substances had been added to the medium and the latter then exposed to natural contamination. The work reported below was performed on pure cultures of organisms isolated from ketchups which were undergoing spoilage, the method adopted for this work being analogous to that employed in testing the strengths of disinfectants.

On examining various ketchups, the predominant type of organism usually found proved to be yeasts, presumably several of the wild species. These undoubtedly find a favorable medium in ketchup, particularly that containing sugar which they ferment with evolution of CO_2 resulting in the characteristic gassy fermentation of many of the spoiled ketchups. Of the bottles examined several were so charged with CO_2 that on opening, the contents were blown out of the bottle in all directions with explosive force. Besides yeasts several organisms of the bacillar type were

from one of the heated ketchups. The predominant flora throughout, however, proved to be yeasts.

After preliminary isolation of these various organisms on an acidified tomato-broth agar, replating and reisolation were performed to insure purity of the cultures. No attempt was made to identify these various organisms by detailed study. They were employed directly to test out the preservative action of cinnamic aldehyde, eugenol, and benzoic acid, respectively. Numerous difficulties were here encountered before a suitable medium and a satisfactory method were devised. The medium finally adopted was a tomato broth bouillon containing 1 per cent sugar and adjusted to 1.5 per cent normal acid. But even with this medium, which gave good growth, it was difficult to test out the action of the various substances above mentioned, owing to the fact that their addition even in minute quantities occasioned a more or less pronounced turbidity which was with difficulty differentiated from that produced by bacterial growth. In several cases it was necessary to make microscopical examinations in order to ascertain whether or not growth had occurred.

Suspensions of the respective organisms were prepared by inoculating tubes of the tomato bouillon and incubating until turbidity had occurred which usually required forty-eight hours. After thorough shaking one loopful of these cultures was transferred to tubes containing 5 cc. of sterile broth. To these were then added varying amounts of cinnamic aldehyde, eugenol, and benzoic acid, respectively, equivalent to 1, 2, 5 and 10 parts per 10,000 of inoculated bouillon. Two tubes of each organism with each of the varying amounts of the different preservatives were prepared. All tubes were incubated at 37°C . and examined daily for three days. The results secured are recorded in Tables VI and VII.

TABLE VI.—INFLUENCE OF PRESERVATIVES UPON GROWTH OF CERTAIN ORGANISMS.

Organism employed.	Day of examination.	Cinnamic aldehyde.				Eugenol.				Benzoic acid.			
		1 pt. per 10,000.	2 pts. per 10,000.	5 pts. per 10,000.	10 pts. per 10,000.	1 pt. per 10,000.	2 pts. per 10,000.	5 pts. per 10,000.	10 pts. per 10,000.	1 pt. per 10,000.	2 pts. per 10,000.	5 pts. per 10,000.	10 pts. per 10,000.
		+	—	—	—	+	—	—	—	+	+	+	—
23d (Spore-former)...	1st day	+	—	—	—	+	—	—	—	+	+	+	—
	2d day	+	—	—	—	+	+	—	—	+	+	+	—
	3d day	+	±	—	—	+	+	±	—	+	+	+	—
5x (Yeast).....	1st day	—	—	—	—	—	—	—	—	+	—	—	—
	2d day	+	—	—	—	—	—	—	—	+	—	—	—
	3d day	—	—	—	—	—	—	—	—	+	—	—	—

TABLE VII.—INFLUENCE OF PRESERVATIVES UPON THE GROWTH OF VARIOUS ORGANISMS

Organism	Cinnamic aldehyde.				Eugenol.				Benzoic acid.		
	5 pts. per 100,000.	1 pt. per 10,000.	2.5 pts. per 10,000.	5 pts. per 10,000.	5 pts. per 100,000.	1 pt. per 10,000.	2 pts. per 10,000.	5 pts. per 10,000.	10 pts. per 10,000.	20 pts. per 10,000.	
5t Yeast.....	+	±	—	±	+	+	—	—	—	—	
23y Bacillus (spore-former).....	+	+	—	—	+	+	+	+	+	+	
23d Bacillus (spore-former).....	+	+	±	±	+	+	+	—	—	—	
23e Blunt bacillus.....	+	+	—	—	+	+	+	+	+	+	
5u Yeast.....	+	±	—	—	+	+	—	—	—	—	
27a Yeast.....	+	+	+	+	+	+	+	+	+	+	
5b Yeast.....	+	±	—	—	+	+	+	—	—	—	
5d Yeast.....	+	±	—	—	+	+	+	+	+	+	
23g Bacillus in chains.....	+	+	+	+	+	+	+	+	+	+	

isolated, and in several bottles of ketchup which had been bottled cold, an organism identical in most respects to the ordinary lactic acid bacterium was found. A large spore-forming bacillus was isolated

From the data submitted it is at once apparent that cinnamic aldehyde possesses a more marked antiseptic action than either eugenol or benzoic acid. Of the two latter, benzoic acid appears to be by far

the least effective as a preservative. In case of cinnamic aldehyde a concentration of 2 parts per 10,000 was sufficient to inhibit the growth of most organisms, only two out of the nine employed showing growth at this concentration. With eugenol 5 parts per 10,000 proved insufficient to prevent the growth of all the organisms tried, four out of nine having grown. Benzoic acid on the other hand revealed a much weaker antiseptic action than either of the above, eight forms out of nine growing in a concentration equivalent to 10 parts per 10,000, and five out of nine in a concentration of 20 parts per 10,000, while three others showed doubtful evidence of growth.

In view of the fact that this work on pure cultures was performed by one of the authors, whereas the work on the apple sauce was performed independently by the other, it is interesting to note that the results in both cases coincide remarkably with one another. For direct contamination of the specially prepared apple sauce, it was found that 0.01 gram of cinnamic aldehyde per 100 grams of sauce (equivalent to 1 part per 10,000) was sufficient to delay growth at least 60 days and that 2 parts per 10,000 prevented all growth, results with which the data in Tables VI and VII correspond very closely. With eugenol the same remarkable coincidence maintains, the results of both observers showing that 10 parts per 10,000 were sufficient to inhibit growth. Thus, both methods, the more practical household method of direct exposure to contamination, as well as the laboratory pure-culture method, yielded identical results in all respects.

In view of the above, it appears that cinnamic aldehyde and eugenol as such possess considerable preservative action and aid materially in preserving substances to which they are added. Both are contained in such spices as cinnamon and cloves. No doubt the marked preservative action of these spices, as shown in the above experiments, must be attributed to their content of these essential oils. As this preservative action takes place, even when the spices are used in the small quantities necessary for flavoring, their use can be recommended in contrast to such spices as pepper and ginger which have been shown to possess but little, if any, preservative action. The more liberal use of cinnamon and cloves in the preparation of ketchup may perhaps remove the necessity of adding sodium benzoate for preserving it, a practice to which there is so much objection.

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THE DETERMINATION OF GLIADIN OR ALCOHOL-SOLUBLE PROTEIN IN WHEAT FLOUR.

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Osborne¹ in his monograph, "The Proteins of the Wheat Kernel," states that the following proteins are present in the wheat kernel: "Gliadin insoluble

in neutral aqueous solutions, but distinguished from all others by its ready solubility in 70 per cent. alcohol; glutinin, a protein having a similar elementary composition to gliadin, soluble in dilute acid and alkaline solutions, and yielding a wholly different proportion of decomposition products when boiled with strong acids; leucosin, an albumin-like protein, freely soluble in pure water, and coagulated by heating its solution to 50–60° C.; a globulin, similar in composition and properties to many globulins found in other seeds, and one or more proteoses which are present in very small quantity."

Osborne states that globulin, albumin and proteose are the proteins found in the embryo of the wheat kernel, while the endosperm consists nearly entirely of gliadin and glutinin. The latter part of this statement of Osborne's is hardly correct, since wheat flour contains considerable proteid material—globulin, albumin and proteose, soluble in dilute salt solution—usually amounting to 10–15 per cent. of the total protein.² However, the proteins of the wheat endosperm do consist very largely of gliadin and glutinin.

The quantitative separation of the proteins of wheat flour is very difficult and not possible of absolute accuracy, since no one protein is entirely insoluble in the solvent used to extract another protein. Thus while a 10 per cent. sodium chloride solution will extract albumin, globulin and proteoses, yet it will also extract some gliadin. Likewise, 70 per cent. alcohol, while presumably extracting only gliadin, also extracts some albumin, globulin, etc. Chamberlain² has done a large amount of work in the quantitative separation of proteins of wheat flour. In his latest report, *Journal of the American Chemical Society*, 1906, he makes, among others, the following conclusions: "As recommended by the author in the Association of Official Agricultural Chemists, the separation of the proteins of wheat into more than two groups, *viz.*, first, alcohol-soluble, second, alcohol-insoluble, seems unwarranted, both because of the difficulty of making a further quantitative separation, and because of the indefinite value of such separation.

In the light of all data available to the writer, this statement of Chamberlain's seems wholly justified. It is to be hoped, however, that methods may be devised by which an accurate quantitative separation of the wheat proteins may be accomplished.

A large amount of chemical investigation has been conducted during the past ten years with wheat flour, and one of the chief objects in this work has been to determine some relation between the composition of the flour and its strength, *i. e.*, ability to produce a large, well piled loaf. An immense number of gliadin determinations have been made in this work, to ascertain if any relation existed between the ration of gliadin to the total protein, and the strength of the flour. The writer proposes to discuss this matter in detail in a later paper.

The determination of gliadin, or to be scientifically

¹ See Chamberlain, *Bull.* 90, p. 124, Bureau of Chem., U. S. Dept. of Agr.

² See Chamberlain, *Bulls.* 81 and 90, Bureau of Chem., U. S. Dept. of Agr.; also Vol. 28, No. 11, *J. Am. Chem. Soc.*

¹ *Proteins of the Wheat Kernel*, pub. by Carnegie Inst., 1907.

correct, alcohol-soluble protein in wheat flour, is simple in principle, and duplicate determinations check very closely. It consists, as usually practised, in frequent agitation for several hours of a weighed quantity of flour with a definite volume of dilute alcohol, letting stand over night, and the final determination of nitrogen in an aliquot portion of the filtrate. As has been mentioned, a single operator can get duplicate determinations to check very closely, and likewise different operators using exactly the same method will get closely agreeing results. Unfortunately, however, the situation is that different chemists use different methods, and hence their results are in no sense comparable, unless the methods used are accurately described, when the results may be compared provided the methods are essentially the same.

Bulletin 107, Bureau of Chemistry, U. S. Dept. of Agr., Official and Provisional Methods of Analysis, Association of Official Agricultural Chemists, contains no method for the determination of gliadin or other wheat proteids. Page 59, Sec. VIII, *Methods for the Analysis of Cereal Foods*, is blank except for the heading.

The chief differences in methods used for the determination of alcohol-soluble protein in wheat flour are these:

1. In the strength of alcohol.
2. In the method of extraction.

What strength alcohol should be used? It is commonly recommended that 70 per cent. alcohol be used, but as a rule the reader is left in doubt as to whether 70 per cent. alcohol means 70 per cent. by weight or 70 per cent. by volume. Seventy per cent. alcohol by weight has a specific gravity of 0.8729 and is equivalent to 76.91 per cent. alcohol by volume. Seventy per cent. alcohol by volume has a specific gravity of 0.8898 and is equivalent to 62.45 per cent. by weight. There is a difference of 6.91 per cent. alcohol by volume or 7.55 per cent. alcohol by weight between alcohol of 70 per cent. strength by weight and 70 per cent. by volume. Provided 70 per cent. alcohol by weight and 70 per cent. by volume extracted the same amount of protein from a flour, one might as well be used as the other. In fact, however, there is a considerable difference in the extractive power of these two strengths of alcohol, as will be shown later.

Just why should 70 per cent. alcohol (whether by weight or by volume) be used instead of alcohol of some other strength, anywhere from 10 per cent. to 95 per cent? Apparently 70 per cent. alcohol has been used on the supposition that it would extract a larger quantity of protein than alcohol of any other strength. Osborne¹ makes the following statement: "Exactly what strength of alcohol dissolves the largest proportion of gliadin has never been determined, but the maximum solubility is attained with about 70 per cent. of alcohol by volume." Without doubt Osborne considers that alcohol of that strength which will extract the largest amount of protein should be used for the determination of gliadin in wheat flour. In the light of all available data, it seems perfectly logical

that alcohol of that strength which will extract the maximum amount of protein should be used for the determination of gliadin in wheat flour.

Some chemists object to using alcohol more dilute than 70 per cent. on the ground that the weaker alcohol extracts the larger proportion of non-gliadin protein. This is a weak objection, since it is a rather difficult matter to determine just what strength alcohol will extract the largest amount of true gliadin and the smallest amount of non-gliadin protein. It would certainly seem best to use that strength alcohol which will extract the largest amount of total protein.

A number of investigators have determined the relative amounts of protein extracted from flour by alcohol of different strengths. Shutt² determined the amount of protein extracted from flour by alcohol varying in strength from 60 per cent. to 75 per cent. by weight, with the following results:

Strength of alcohol by weight. Per cent.		Gliadin. Per cent		Proportion of protein in the form of gliadin.
60		5.36		54.0
62.5		5.30		53.4
65.0		5.24		52.9
70		4.71		47.4
75		3.41		34.3

From this data it will be noted that there is a constant decrease in the amount of protein extracted as the alcohol increases in strength from 60 per cent. to 75 per cent. by weight. Since 60 per cent. alcohol is the lowest strength shown there is no means of knowing just what strength of alcohol would extract the largest proportion of protein.

Sixty-two and five tenths per cent. alcohol by weight corresponds closely with 70 per cent. by volume. By looking at the above table it will be noted that 70 per cent. alcohol by weight extracts 0.59 per cent. less protein than 62.5 per cent. by weight, or 70 per cent. by volume. The gliadin number with the 70 per cent. alcohol by weight is 47.4, while with 70 per cent. alcohol by volume it is 53.4. Obviously it makes considerable difference whether alcohol used for the determination is 70 per cent. by weight or by volume, or whether alcohol of some different strength is used. Shutt makes special mention of the fact that alcohol used for the determination of gliadin should be prepared with great accuracy, since, as his results show, slight differences in strength of the alcohol materially affect the amount of protein obtained. The above writer uses 70 per cent. alcohol by weight for the determinations reported in that bulletin.

Snyder³ in his report on the separation of vegetable proteins before the Association of Official Chemists, 1906, makes reference to several investigations conducted to determine what strength of alcohol would extract the maximum amount of protein from wheat flour. Teller, of the Arkansas Station, determined the amount of protein extracted from flour by alcohol varying in strength from 40 per cent. to 95 per cent., with the following results:

¹ *Bull. 57*, Central Experimental Farm, Ottawa, Can., 1907.

² *Bull. 105*, Bureau of Chem., U. S. Dept. of Agr.

³ *Proteins of the Wheat Kernel*, pub. by Carnegie Inst., 1970, p. 109.

AMOUNT OF NITROGEN DISSOLVED BY VARYING STRENGTHS ALCOHOL.

Alcohol by volume. Per cent.	Alcohol-sol- uble nitrogen. Per cent.	Alcohol by volume. Per cent.	Alcohol-sol- uble nitrogen. Per cent.
95	0.21	65	1.30
90	0.31	60	1.38
85	0.61	55	1.40
80	0.89	50	1.40
75	1.08	45	1.40
70	1.18	40	1.40

It will be noted that the maximum extraction was obtained with 40-55 per cent. alcohol by volume.

Snyder determined the amount of protein calculated as nitrogen extracted by alcohol, varying in strength from 60-70 per cent. by weight, with the following results:

PROTEIN CALCULATED AS NITROGEN DISSOLVED BY 60-70 PER CENT. ALCOHOL.

Alcohol.	Per cent.	Nitrogen.	Per cent.
	60	0.85	
	68	0.74	
	70	0.70	
	72	0.67	

Shutt also reports results obtained with alcohol varying in strength from 60 to 86.4 per cent. by weight, the amount of protein extracted decreasing with the increase in strength of alcohol. The results are as follows:

GLIADIN NITROGEN DISSOLVED BY VARYING STRENGTHS ALCOHOL.

Alcohol. Per cent. by weight.	Gliadin nitrogen. Per cent.	Alcohol. Per cent. by weight.	Gliadin nitrogen. Per cent.
60	0.94	75	0.60
62.5	0.93	76.8	0.66
65	0.92	86.4	0.12
70	0.83		

On looking over all available data, it appears that Teller is the only one who has determined the solvent power of alcohol of less strength than 60 per cent. by weight. He finds that the protein extracted by alcohol varying in strength from 40-55 per cent. by volume is practically constant. The other investigators find a gradual decrease in solvent action of alcohol as it increases in strength above 60 per cent. While Teller's work appears conclusive, it was thought worth while to cover the ground even more fully, both as regards strength of alcohol and the method of extraction, in order to obtain the maximum amount of gliadin from flour. The following points were investigated:

1. Time necessary for maximum extraction.
2. Strength alcohol necessary for maximum extraction.
3. The effect of temperature on the determination of gliadin.

The common method for the determination of gliadin is to extract 2 grams of flour with 100 cc. neutral alcohol in a glass or rubber stoppered flask for 18 to 24 hours, shake frequently the first three to four hours, then allow to stand over night, filter and determine nitrogen in an aliquot portion of the filtrate in the usual manner. This method is undoubtedly accurate provided the flask is shaken frequently for some time. The only objection is the time element. In commercial laboratories, where immediate results

are wanted, time is an element of considerable importance.

This laboratory is provided with a soil shaker used for the mechanical analysis of soils. It has compartments for 16 8-ounce milk sterilizer bottles, has a backward and forward movement, and is run by a $\frac{1}{4}$ h. p. motor. The following experiment was conducted with macaroni flour to determine the length of time necessary, with constant shaking, to affect a complete extraction of gliadin from flour,

Approximately 5 grams of flour were weighed into each of five sterilizer bottles; 200 cc. neutral 70 per cent. alcohol by weight added. Four bottles were placed in the shaker, and shaken for periods of 30, 45, 60 and 90 minutes respectively. The fifth bottle was shaken by hand at intervals for three hours, and then let stand over two days, making forty-seven hours in all. In the case of samples run in the shaker, filtration was facilitated by running the samples for ten minutes in an electric centrifuge, which gave a clear solution which hardly needed filtering. Nitrogen was determined in filtrate by the modified Kjeldahl method.

GLIADIN EXTRACTED ON SHAKING FOR DIFFERENT PERIODS.

Sample.	Time shaken.	Per cent. gliadin N extracted.
1	30 min.	0.90
2	45 min.	0.95
3	60 min.	0.96
4	90 min.	1.03
5	Shook frequently for 3 hrs., let stand 44 hrs.	0.97

A similar test was run with a sample of soft winter wheat flour, using 70 per cent. alcohol by weight, with the following results:

Sample.	Time shaken.	Per cent. gliadin N extracted.
1	60 min.	0.89
2	90 min.	0.90
3	Shook frequently for 3 hrs., let stand 15 hrs.	0.84

In the first test, shaking for 90 minutes gives slightly higher results than shaking for 60 minutes. Shaking for 60 minutes gives practically identical results with the method (No. 5) where the sample is shaken for 3 hours and let stand over night or longer. In test No. 2 practically identical results are obtained where samples are shaken for 60 and 90 minutes respectively. Sample No. 3, using the old method, gives slightly lower results than the first two samples.

These tests show that alcohol-soluble protein can be as completely extracted from flour by shaking the sample vigorously for 60-90 minutes in a shaking machine, as when the sample is shaken frequently for two to three hours by hand, and then let stand 18 hours more or less.

The method now in use in this laboratory for the determination of alcohol-soluble protein in flour is as follows: weigh approximately 2 grams of flour into an 8-ounce milk sterilizer bottle, add 100 cc. neutral 50 per cent. by weight alcohol; shake in machine for one hour, centrifuge for ten minutes, filter, determine nitrogen in aliquot portion of filtrate by modified Kjeldahl method. Correction is always made for a

blank determination run with the alcohol, etc. In using a shaking machine it is, of course, necessary to have the bottles shaken vigorously so that the flour will remain in suspension. The use of the centrifuge makes filtration easy, which would otherwise be rather slow, due to fine flour particles in suspension.

In making up the varying strengths of alcohol reported in this paper, the alcohol table found in Leach was used, and the specific gravity was determined by means of a Sartorius balance. The making up of a definite strength alcohol for the determination of gliadin is a matter of considerable importance. An accurate Westphal or Sartorius balance, or pycnometer, should be used, and not a spindle. The temperature at which the reading is taken should of course be exactly that for which the alcohol table is intended.

THE EFFECT OF TEMPERATURE ON THE EXTRACTION OF GLIADIN FROM FLOUR.

Opinion differs as to the relative solvent action of cold or boiling alcohol on flour.

Leach¹ gives a method for the determination of gliadin which consists in shaking 1 gram of flour with 100 cc. 75 per cent. hot alcohol, and keeping the mixture at a temperature just below the boiling point of the alcohol for one hour, shaking frequently. The mixture is then filtered and nitrogen determined in the usual way.

Chamberlain² reports results showing that cold alcohol extracts more gliadin from flour than hot alcohol.

The following tables show the results of a test conducted in this laboratory to determine the amount of protein extracted by 50 per cent. by weight alcohol at different temperatures.

Approximately 2 grams of flour were weighed into each flask, 100 cc. of cold 50 per cent. by weight alcohol added, single tube condensers inserted and each flask placed in a water bath at the desired temperature. Samples were shaken frequently during the period of extraction, and were finally allowed to cool before filtering. A baker's patent spring wheat flour was used.

TEST No. I.

Sample No.	Temperature.	Period of extraction.	Per cent. of gliadin nitrogen.
1	35-37° C.	4 1/2 hrs., then let stand 14 hrs.	1.20
2	50	2 1/4 hrs., then let stand 14 hrs.	1.19
3	60	2 1/4 hrs., then let stand 14 hrs.	1.23
4	75	2 1/4 hrs., then let stand 14 hrs.	1.45
5	75	2 1/2 hrs., then let stand 14 hrs.	1.58
6	25-27	Shake 1 hr., usual method	1.18

(Test No. 5 made at a different time from Test No. 4.)

From this table it appears that there is no increase in the amount of gliadin extracted with rise in temperature, until a temperature just below that at which the alcohol boils is reached. The two samples extracted at 75° C. at different times gave quite different results. Extracting with hot alcohol is more difficult of operation and does not seem to offer any advantage over extracting in the cold. Unless

all extractions are carried on under exactly the same conditions, extraction with hot alcohol probably will not give as accurate results as our present methods.

AMOUNT OF PROTEIN EXTRACTED FROM FLOUR WITH ALCOHOL OF VARYING DEGREE OF STRENGTH.

The following table reports results of tests run to determine the relative solvent action on wheat protein, of alcohol varying in strength from 10 per cent. to 75 per cent. by weight; and including one extraction with distilled water. The method used for all determinations is the one previously described as being used in this laboratory, all tests being run under exactly the same conditions except as regards strength of alcohol.

RELATIVE EXTRACTIVE POWER OF ALCOHOL OF VARYING STRENGTHS

Alcohol by weight. Per cent.	Hard Spring Baker's patent. Per cent. gliadin nitrogen.	Soft Winter patent. Per cent. gliadin nitrogen.
Water.	0.60	0.51
10	0.56	0.46
20	0.57	0.50
30	0.99	0.78
35	1.13	0.92
40	1.16	0.93
45	1.17	1.02
50	1.18	1.03
55	1.13	0.99
60	1.12	0.96
65	0.96	0.87
70	0.90	0.87
75	0.61	0.54

From this table it will be noted that alcohol of 10-20 per cent. strength extracts less protein than distilled water, and that as alcohol increases in strength from 10 per cent. to 50 per cent., it extracts more protein. Alcohol varying in strength from 45 per cent. to 55 per cent. extracts practically the same amount of protein. As the alcohol increases in strength from 55 per cent. to 75 per cent. its solvent action decreases, the drop being more rapid as the alcohol increases in strength. Seventy-five per cent. alcohol extracts about the same amount of protein as distilled water.

The results of this work confirm the work of Teller, who found that alcohol of from 40 per cent. to 60 per cent. by volume extracted the most protein from wheat flour, and there appears to be no logical reason why alcohol of 70 per cent., whether by weight or volume, should be used for the determination of gliadin, or alcohol-soluble protein in wheat flour. On the other hand, since alcohol of 50 per cent. strength by weight extracts as much or more protein than alcohol of any other strength, it would seem perfectly logical that 50 per cent. by weight alcohol should be generally used for the determination of alcohol-soluble protein in wheat flour.

As a result of work reported in this paper the following conclusions seem justified.

1. For the determination of alcohol-soluble protein in wheat flour, shaking the sample vigorously and continuously for 60 to 90 minutes in a machine, or otherwise, gives equally as high results as when the ordinary method, covering a period of from 18 to 24 hours, is followed.

2. While boiling alcohol extracts slightly more pro-

¹ Food Insp. and Anal., 1st Ed., p. 232.

² J. Am. Chem. Soc., No. 11 (1906).

tein than cold alcohol, there does not appear to be any advantage in its use.

3. Alcohol varying in strength from 45 per cent. to 55 per cent. by weight extracts more protein than alcohol of any other strength, hence it is recommended that 50 per cent. by weight alcohol be used for the determination of gliadin in wheat flour, and that the use of 70 per cent. alcohol, whether by weight or by volume, be discontinued.

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THE DETECTION OF BENZOIC ACID IN COFFEE EXTRACT.

By HERMAN C. LYTGOE AND CLARENCE E. MARSH.

Received July 21, 1911.

In testing a sample of coffee extract for benzoic acid by extracting with ether and testing the ether extract in the usual way with ferric chloride, a precipitate was obtained corresponding to ferric benzoate except in color, but on subliming this precipitate the crystals did not have the characteristic appearance of benzoic acid. A portion of the original sample was then acidified with phosphoric acid and subjected to distillation with steam. The distillate was made alkaline with sodium carbonate, evaporated to about 50 cc., acidified, extracted with ether, and the ether extract was extracted with ammonia. The ammoniacal solution was then evaporated until free from ammonia and ferric chloride was added which produced a precipitate with the same characteristics as in the previous instance.

A sample of coffee extract was then made from pure coffee, and upon repeating these tests this extract was found to act the same as the commercial extract. A large number of coffee extracts were made from different varieties of coffee and in all cases they reacted in the same manner.

The ammonium salt of this substance which was extracted with ether was found to give precipitates with salts of manganese, nickel, magnesium, calcium, and barium, as well as salts of iron and copper, while benzoates will produce precipitates only with salts of iron and copper, and from these differences the following

method for the detection of benzoic acid in coffee extract has been devised:

Make the solution acid and extract several times with ether. Wash the combined ether extracts with water and extract with ammonia. Evaporate the ammoniacal extract to a small volume, adding ammonia from time to time to prevent it from becoming acid, and add a solution of manganese sulphate. Filter through a small filter, wash with as little water as possible and add ferric chloride to the filtrate when a dark greenish precipitate will occur if benzoic acid is present. Evaporate to dryness in the casserole in which the precipitation was made, and sublime by placing an inverted funnel covered with a filter paper in the dish and heating over an asbestos gauze. Remove the funnel, and determine the melting point of some of the crystals which, if benzoic acid, should be 121.4° C. The rest of the crystals may be dissolved in ammonia, the excess of ammonia evaporated and ferric chloride added, when the characteristic flesh-colored precipitate will occur if benzoic acid is present.

For quantitative purposes the method of Edmund Clark¹ was employed with good results as the natural reacting substance has but little influence. Determinations made on pure extracts by this method gave from 0.01 to 0.04 per cent. benzoic acid and a correction can be readily made if desired.

The accompanying table gives the analyses of a sample of coffee extract made in the laboratory and of two commercial extracts, one of which contained benzoic acid and glycerine, being very deficient in coffee:

ANALYSES OF COFFEE EXTRACTS.

	Specific gravity, 150.	Solids. Per cent.	Ash. Per cent.	Reducing sugars. Per cent.	Nitrogen. Per cent.	Caffeine. Per cent.	Sodium benzoate. Per cent.
Made in laboratory..	1.059	13.56	2.50	0.22	0.36	0.67
Commercial.....	1.057	13.40	2.29	0.17	0.42	0.70
Commercial.....	1.070	21.42	0.93	0.58	0.15	0.14	0.19

DEPARTMENT OF FOOD AND DRUG INSPECTION.
MASSACHUSETTS STATE BOARD OF HEALTH,
BOSTON.

PLANTS AND MACHINERY

THE THOMAS GAS METER.

By H. N. PACKARD.

Received September 5, 1911.

The application of the electric meter to commercial measurement of gases first suggested itself to Professor Carl C. Thomas while carrying on extensive experiments on the specific heat of superheated steam at Sibley College and the University of Wisconsin. These investigations required the use of some form of heating device. The difficulty of direct quantitative measurements of heat except by electrical measuring instruments finally required the adoption of electric heaters. The great convenience of these heaters in this work led to a series of tests on the measure-

ment of different gases demonstrating the practicability of the method for commercial purposes.

The reasoning on which the operation of the meter is based is this: The specific heat of most gases is a quantity already accurately determined and it is known that this value changes but slightly through wide ranges of temperature and pressure. If an electric heater be placed in a pipe line through which there is a constant flow of gas, and the heater give off heat at a constant rate, the gas temperature is raised a certain fixed amount. Any change in gas flow under these conditions will mean a change in its temperature increase, an increase in gas flow

¹ Science, Aug. 20, 1909, p. 253.

causing a decrease in temperature difference while a smaller gas flow causes an increase in temperature difference; that is, the temperature change of the gas with constant heater input is inversely proportional to the rate of flow. The natural development with these facts in mind was the use of a graphical temperature recorder to show the change of temperature difference as the gas flow varied, and while a constant quantity of heat was being added. While this method gave a measure of the gas flow it was not entirely satisfactory from a commercial standpoint as the temperature charts could not be readily integrated to give readings directly in cubic feet. The next step from constant heat input with variable temperature range was to constant temperature difference with

Let Q = cubic feet of gas per hour at some standard condition.

E = energy in K. W.

3412 = B. T. U. equivalent of 1 K. W. hour.

T = temperature range through which gas is heated.

S = specific heat at constant pressure of the gas, per cubic foot.

Then $Q = 3412E/TS$.

CONSTRUCTION OF THE METER.

The meter in commercial form consists essentially of two parts: first, a means for adding heat; second, thermometers for regulating the temperature rise due to the addition of this heat. For the heater an electric resistance, B, Fig. 1, is used of such a form

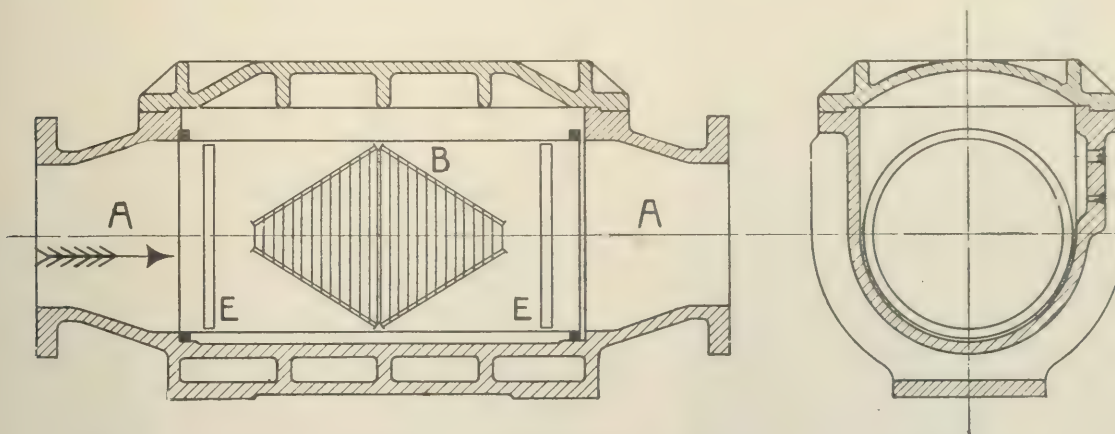


Fig. 1.—Sectional view of meter casing showing heater (B) and thermometers (E).

variable heat input. In this form a satisfactory commercial meter was developed.

In the commercial meter by means of an automatic control the input to the heater is made to vary with the quantity of gas flowing in such a way as to keep the temperature range through which the gas is heated a constant quantity. That the watts input to the heater gives a direct measure of the weight of gas flowing will be shown in the following example: A commonly accepted value for the specific heat of air at constant pressure is 0.2375 B. T. U. per pound. Expressing this value in watts, we have directly the watts required to raise the temperature of one pound of air one degree F. As this is not the most convenient form for commercial work where the unit desired is the cubic foot at some standard condition, we may use the specific heat per cubic foot at that condition instead of the specific heat per pound and obtain the watts required per cubic foot to raise the air temperature one degree. As the watts used by the heater are in direct proportion to the gas flow, the wattmeter may be calibrated to read directly in cubic feet of gas at standard conditions. To sum up, the meter measures the gas in units of weight, not volume. Thus the pressure and temperature of the gas measured have no influence on results. If the weight per standard cubic foot of gas is known, the meter can be calibrated to give readings directly in this form. The action of the meter may be expressed by the following simple formula:

as to distribute the heat evenly throughout the gas. Its current consumption is measured by graphical and recording wattmeters. The thermometers E, Fig. 1, are of the electric resistance type built in the form of a screen of small enough mesh to give an almost perfect average of the gas temperature over the whole section of a pipe, no matter how unevenly the gas flow is distributed. They are placed one on each side of the heater, measuring the difference in temperature between the incoming and outgoing gas. The thermometers and the heater are contained in a casing that is slipped into a section of the pipe line. The heater has an automatic controlling rheostat that allows a sufficient current to flow through the heater to maintain a constant temperature difference between the two thermometers of about two degrees F. On a switchboard at any convenient distance from the pipe line (Fig. 2) are mounted the wattmeters and the automatic heater control device. The heater rheostat control is operated through a Wheatstone bridge galvanometer (Fig. 3), two legs of the bridge being made up of the two thermometers, the other two being standard coils with zero temperature coefficient. The thermometer resistances T_1 and T_2 (Fig. 3) are adjusted to make them as nearly equal as possible when at the same temperature, the final adjustment being made by a small rheostat in the bridge circuit for exact balance, with gas flowing through the meter. The temperature coefficient of the thermometer wire being accurately known, a small resistance equivalent

to the change in temperature resistance for a two degree rise in temperature is placed in series with the entrance thermometer. Now the system is unbalanced unless heat is added by means of the heater, suffi-

cient to raise the temperature of the exit thermometer exactly two degrees, thus making its resistance equal to the entrance thermometer plus the temperature coil resistance.

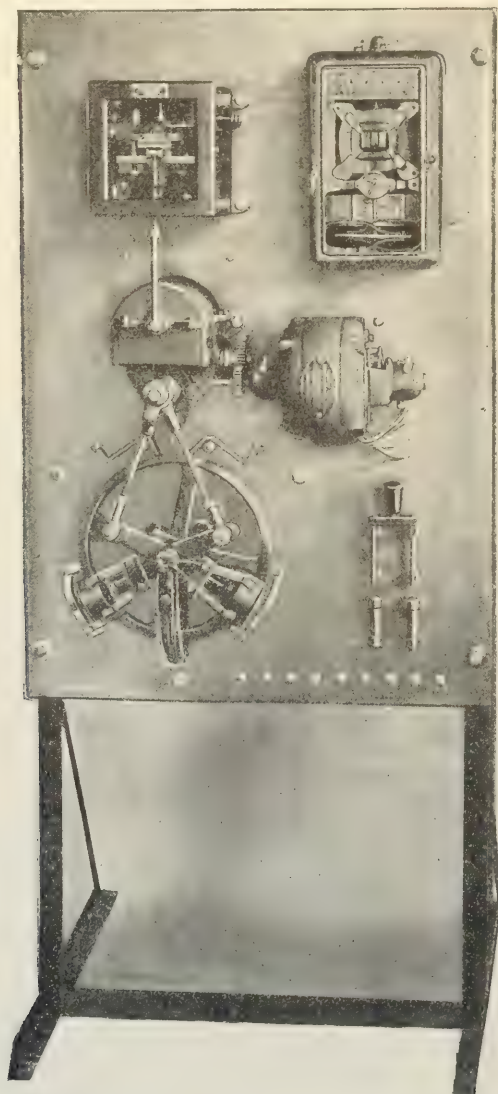


Fig. 2.—Switchboard showing heater control device and recording wattmeter.

cient to raise the temperature of the exit thermometer exactly two degrees, thus making its resistance equal to the entrance thermometer plus the temperature coil resistance.

On the switchboard is mounted a small motor which drives by means of suitable gearing a drum controller, D, having the crank C on the end of its shaft, and at the same time gives the bell cranks on which pawls P and P_1 are mounted a motion sufficient to cover three teeth on the ratchet wheel W. The crank C gives the plate B a short motion to clamp the bridge galvanometer needle N between B and the contact plate shown above it at short time intervals. The ratchet wheel W and the control arm for the heater rheostat R_h are both keyed on the shaft S, so that any change in position of the ratchet wheel changes the resistance of the rheostat. As this

ACTION OF THE METER.

In Fig. 3 is shown a sectional view of a gas main with thermometers T_1 and T_2 on each side of the heater coil. An increase in gas flow will cause the thermometer T_2 to become cooler than its normal two degrees above thermometer T_1 and decrease its resistance. This throws the bridge galvanometer out of balance, the galvanometer needle N moving to the right. The plate B now clamps N between itself and one of the contacts above according to the deflection of N. Suppose the third contact is made. As soon as N is clamped the controller D makes contact at 3 energizing a solenoid that draws pawl P_1 into the ratchet wheel when P_1 is at the bottom of its stroke. The motion of the bell crank causes P_1 to move the ratchet wheel three teeth, cutting out some of the rheostat resistance R_h and allowing more current to flow through the heater. If the needle N had been clamped at the second contact the controller D would have made the circuit through contact finger 2, and P_1 would have caught only two teeth on the wheel W. If the gas flow had decreased the needle N would have been thrown to the left and pawl P would have been thrown into action, moving W in the opposite direction, thus increasing the resistance of the rheostat. By means of this

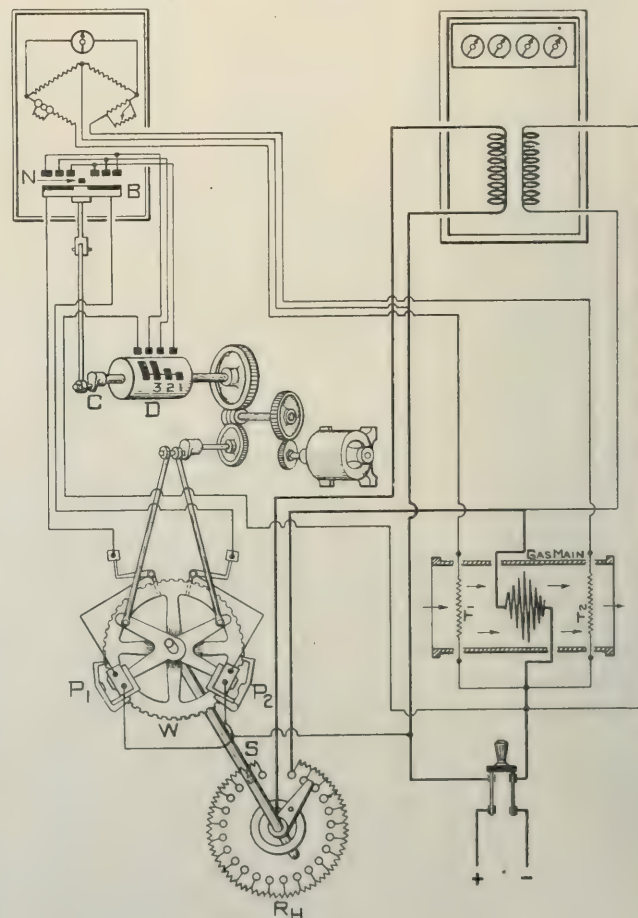


Fig. 3.—Diagram of meter.

device the proper amount of energy is allowed to be dissipated in the heater to maintain a two-degree temperature difference between thermometers T_1 and T_2 . Any change in the bridge galvanometer needle from its balanced position, due to change of the proper temperature range between T_1 and T_2 , causes a corresponding change in the heater energy.

COMMERCIAL REQUIREMENTS OF A METER.

For a meter to be successful commercially there are several essential requirements. Accuracy, large range, freedom from interference with operation by deposits from the gas and a reasonable cost of operation are perhaps the most important. Most forms of commercial meters will work within 2 per cent. of correct values when properly adjusted and calibrated and when within the range of measurement for which they are designed. While this is true when first installed, after a long period of operation calibration is necessary to prove accuracy. With most meters this means a removal from the line with a consequent interruption of service. With the Thomas meter this checking for error may be accomplished in a few moments' time without disturbing it at all. The operation is as follows: the heater circuit is broken and the temperature difference coil in the Wheatstone bridge is shorted out. This should leave the bridge in perfect balance, as the two thermometers if properly made have exactly the same resistance at the same temperature. If not in balance, by means of the bridge adjusting rheostat already described, this balance may be restored. Now that the thermometers are known to be of the same resistance the only chance of error is in the temperature resistance coil and the electrical measuring instruments. The resistance coil is so made that an appreciable change in the resistance is impossible. The wattmeters can be calibrated by placing instruments of known accuracy in series with them.

With most meters deposits from the gas are likely to affect their accuracy somewhat. With the electric meter the only effect is to change the speed of the thermometers, the increased mass making them slower to respond to temperature fluctuations. A deposit does not seriously affect the accuracy, only making the instrument slow to register rapid change of flow.

The Thomas meter normally covers a range of 15 to 1 accurately, but by a slight adjustment this range can be increased to about 60 to 1. To do this two temperature difference coils are used. For high range work the gas is heated only two degrees while for the low range a 5- or 10-degree temperature difference is maintained. This requires that the wattmeter readings for the low range be divided by the ratio of the two temperature differences to give the true readings.

The only maintenance charge against the meter is the cost of the operating current. A kilowatt hour will measure about 75,000 cubic feet of free gas, thus making the current cost less than one-fourth of one per cent. of the value of the gas measured, an extremely small item when it is considered that

the accuracy usually expected of commercial meters is not better than one per cent. Except for oiling bearings and changing charts on the graphical meter, no attendance is required. All results are direct in standard cubic feet, with no laborious computations or corrections for temperature and pressure.

ERRORS DUE TO VARIATION OF GAS COMPOSITION.

In the formula $Q = 3412 E/ST$, E and T are fixed for a given gas flow, leaving the only theoretical source of inaccuracy in the value of S . The conditions affecting the accuracy of S , the specific heat at constant pressure, are chiefly variation of moisture content, and variation of the composition of the gas to be measured.

The moisture correction would be maximum with a saturated gas. Taking the case of air at 60 degrees F., 30 inches barometric pressure, the weight per cubic feet of the saturated air is 533 grains. The weight of the vapor contained in it is 5.6 grains or 1.05 per cent. of the total. As the specific heat of the aqueous vapor is about twice that of air, the specific heat of saturated air is about one per cent. higher than that of dry air for these conditions. In the measurement of gases such wide variations in moisture content are seldom met with and in most instances can be entirely neglected without appreciable error. In any case, if desired, a correction may be made for moisture content.

The second source of error, that due to variation of specific heat with variable gas composition, actually works out to give very small errors as the constituents of the gas liable to variation are such as to have but small effect on the specific heat, as the following example will show.

A typical city gas is made up of a mixture of coal and water gas, the proportions of this mixture varying through wide ranges. Below are given sample analyses of the two gases, the specific heats of each computed from the analyses, and the specific heats of various mixtures of the gases.

	Water gas.	Coal gas.
CO ₂	3.8	2.2
C ₂ H ₄	12.3	3.3
O.....	0.6	0.5
CO.....	30.4	6.9
H.....	33.3	50.6
CH ₄	14.4	34.2
N.....	5.2	2.3

From these analyses the following values of specific heat are computed for different mixtures.

Water gas. Per cent.	Coal gas. Per cent.	Specific heat.
100	0	0.02094
90	10	0.02096
80	20	0.02098
70	30	0.02100
60	40	0.02102
50	50	0.02104
40	60	0.02106
30	70	0.02108
20	80	0.02110
10	90	0.02212
0	100	0.02114

The above values of specific heat are in B. T. U. per degree F. for a cubic foot of gas at 14.804 pounds absolute pressure and 60 degrees Fahrenheit.

As may be seen from this table the maximum error when changing from 100 per cent. coal gas to 100 per cent. water gas is slightly less than one per cent. The average error would be much less than this. Corrections can be made as desired if frequent analyses are obtained, but in general an average gas composition can be determined for which the specific heat can be computed, giving results over a period of time that are extremely close to the true value.

Excess of moisture in the form of a finely divided spray causes some inaccuracy in results. This may be overcome by use of a separator or a heater to bring the gas above the saturation point, or better still installing the meter in a part of the line where such troubles cannot occur.

with a large wet meter of known accuracy on both gas and air, and curves plotted from the test results between cubic feet of gas flow per hour and degrees rise in temperature.

It was desired to compute the specific heat of a gas by means of a test based on the following reasoning:

Let G = cubic feet of gas per hour.

E = energy in kilowatts.

3412 = B. T. U. equivalent of 1 K. W. hour.

S = specific heat per cubic foot.

Then GST = heat energy equivalent to E or.

$GST = 3412 E$.

$GT/E = 3412/S =$ a constant K , this depending on the value of S .

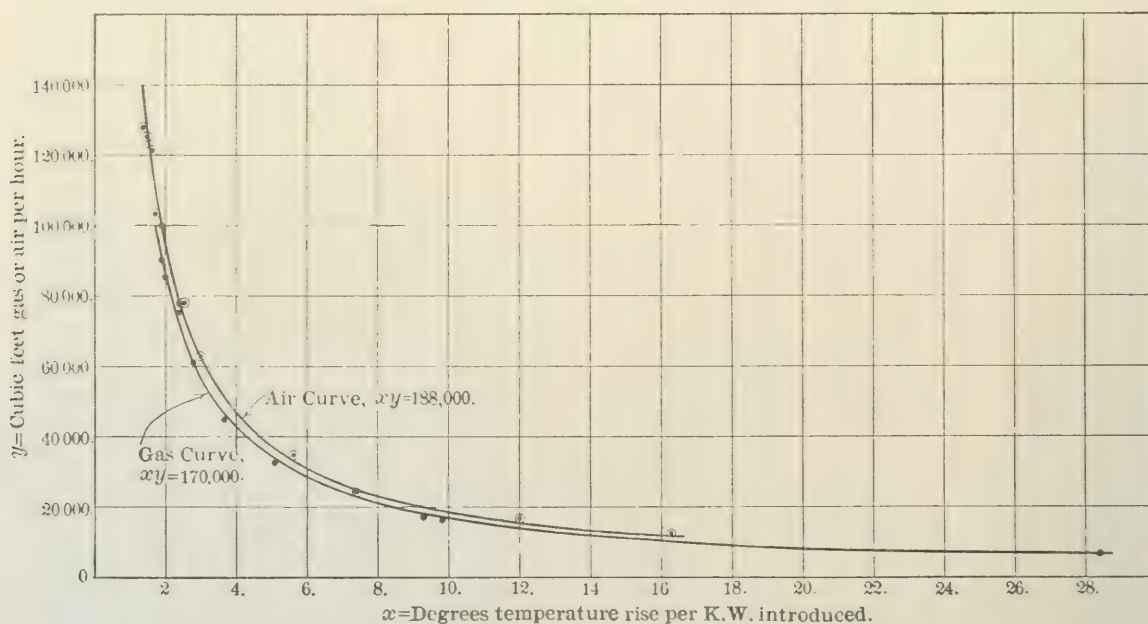


Fig. 4.—Curves showing graphically the results of tests on air and gas measurement.

LABORATORY TESTS.

A number of tests were carried out recently at the University of Wisconsin with three types of meters in series on a pipe line, measuring air. The meters used were the Venturi meter, Pitot tubes and a Thomas meter of a crude form having a hand-controlled heater.

Simultaneous readings were taken for each meter with different rates of air flow. These three instruments, whose design depends on as many different theories, gave results checking each other within small limits, proving the accuracy of the reasoning involved in each case. The electric meter gave results directly in standard units, and with the same degree of accuracy even in a crude form that required laborious computations and extremely careful manipulation with the other two types.

COMMERCIAL TESTS.

1. *Artificial Gas and Air.*—A test made on this meter during the development work on artificial gas and air gives an interesting check on the correctness of its design. The meter was operated in series

In Fig. 4 the curves are plotted with values of G , (cubic feet of gas per hour) as ordinates and T/E (degrees rise per kilowatt expended in the heater) as abscissas. Since $G \times T/E =$ a constant, these curves are rectangular hyperbolas. That these curves are asymptotic to the co-ordinate axes is evident from the fact that an infinitely large mass of gas would have its temperature increased an infinitely small amount by any finite amount of heat, while at the other extreme a finite amount of heat will cause an infinite rise in temperature to an infinitely small mass of gas.

In the commercial meter the value of T is kept constant. Then K/T will be a constant. Let its value be C . This gives $G = KE/T = CE$.

From the gas curve (Fig. 4) which was made with illuminating gas at an average temperature of 59 degrees F. and an average absolute pressure of 6 inches of water plus 29.8 inches of mercury, the value of the constant K is found to be 170,000. But $K = 3412/S = 170,000$. Then $S = 3412/170,000 = 0.0201$. Reducing this value to standard conditions of 32 degrees F. and 29.9 inches mercury it becomes 0.0210, which is to be compared with the calculated

specific heat of 0.0211. The analysis of this gas and the computation for its specific heat is given below.

	Vol. cu. ft.	Weight per cu. ft., lb.	Total weight, lb.	Specific heat per lb.	Specific heat per cu. ft.
CO ₂	0.04	0.11637	0.004658	0.216	0.00100
C ₂ H ₄	0.11	0.0741	0.00815	0.404	0.00329
O ₂	0.001	0.08463	0.00085	0.217	0.00002
CO.....	0.331	0.07407	0.02450	0.245	0.00600
CH ₄	0.1761	0.04234	0.00746	0.593	0.00442
H ₂	0.303	0.00530	0.00160	0.409	0.00546
N ₂	0.0389	0.07429	0.00289	0.244	0.00071
				0.02090	

For the air curve $K = 188,000$ and $S = 3412/188,000 = 0.0181$, or at 32 degrees and 29.9" mercury, 0.0191. The accepted specific heat of air for these conditions is 0.0192.

Fig. 5 shows a typical installation in an artificial gas plant. This meter has a capacity of 3,000,000 cubic feet of free gas per hour and an accurate minimum capacity of 50,000 cubic feet per hour. The switch-board with the recording and graphical wattmeters and the controlling galvanometer is located on the station floor while directly below in the basement is the heater rheostat and operating motor. The meter

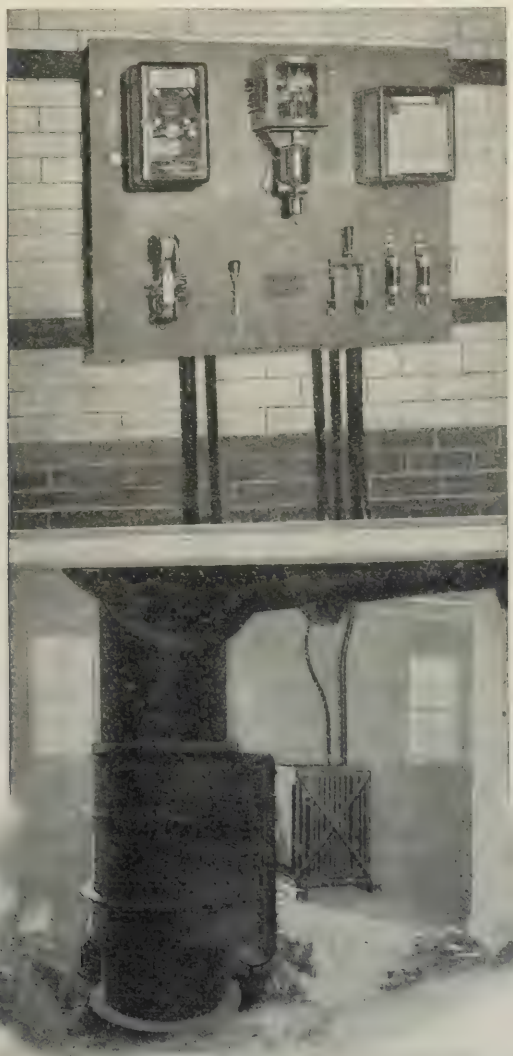


Fig. 5.—A Thomas meter installed in a city gas plant.

casing forms a short vertical section of the 30-inch gas main shown in the cut. Fig. 6 is a reproduction of a graphical chart taken by this meter, showing the noon peak load.

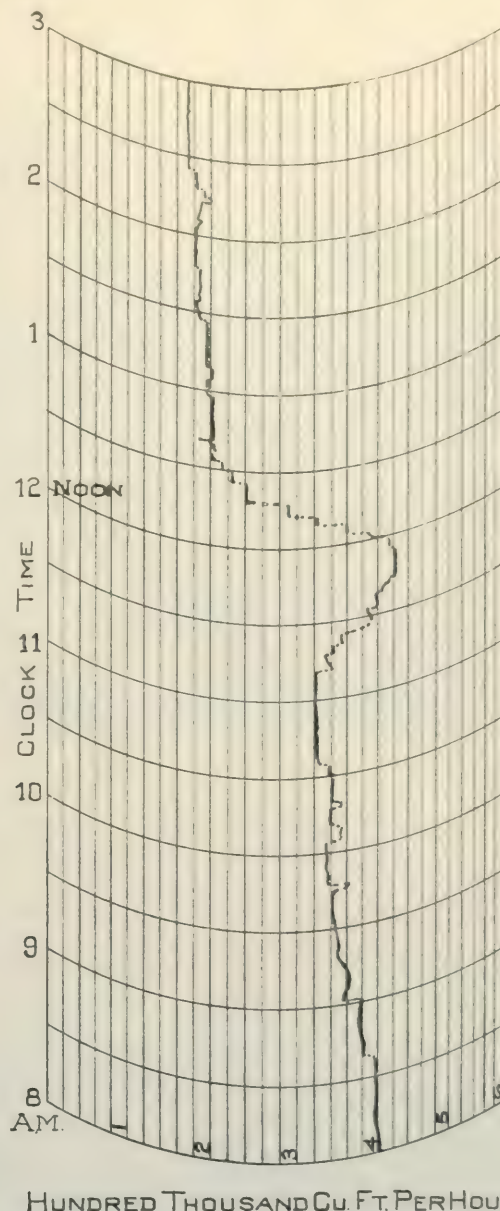


Fig. 6.—Graphical chart taken by meter shown in Fig. 5.

2. *Natural Gas Tests.*—Recently a series of tests have been carried on with a Thomas meter at the Brave Station of the People's Natural Gas Company, of Pittsburgh. The meter is in series with a carefully calibrated Pitot tube station in a line where pressures vary from 50 to 200 pounds gauge and temperatures vary with weather conditions. About a mile and one-half of 10-inch pipe separates the two meters. The Thomas meter (Fig. 7) is installed in a field immediately between two elbows and close to gate valves, within 200 ft. of the suction header in the pumping plant. The variations in pressure, due to the action of the pumps and the bad eddy currents formed in the gas by the valves and elbows,

give the meter a severe test. Fig. 8 shows the meter panel with recording instruments and heater rheostat on the station floor, to the right of the lighting plant switchboards. The meter has a maximum capacity of 750,000 cubic feet of free gas per hour and a minimum accurate capacity of 12,500 cubic feet, and gives readings directly in standard cubic feet per hour at

Readings were taken at the Pitot tube station, of pressure and velocity head, every 15 minutes day and night and the results reduced to 15.025 pounds absolute and 60 degrees F. by carefully prepared tables. The results were thus directly comparable to the Thomas meter readings. The chart readings for the electric meter were found by averaging the curve

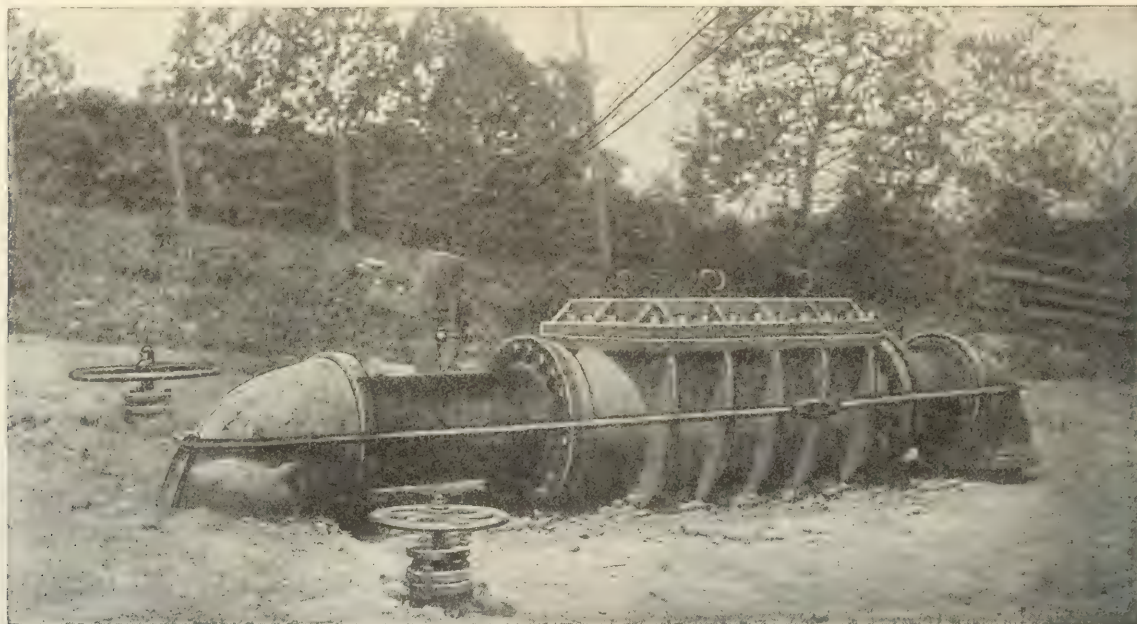


Fig. 7.—An installation in the natural gas fields.

15.025 pounds per square inch, absolute, and 60 degrees F., the specific heat for this condition being calculated from an assumed average analysis. Two tests were made, the first a twenty-two hour test with nearly constant gas flow and temperature but with pressures ranging from 72 to 123 pounds gauge; the second a forty-five day run under service conditions.

traced by the graphical wattmeter. Hourly readings were taken from the integrating wattmeter. The following table gives the results of the 22-hour run under test conditions.

HOURLY RESULTS OF 22-HOUR TEST OF THOMAS METER.

Hour.	Cubic feet each hour.			Total cu. ft. at end of each hour.		
	Chart.	Integrating-meter.	Pitot tube.	Chart.	Integrating-meter.	Pitot tube.
8-9	397500	400000	400297	397500	400000	400297
9-10	398500	398000	394027	796000	798000	794324
10-11	370000	374000	373731	1166000	1172000	1168055
11-12	376500	277000	380800	1542500	1549000	1548855
12-1	361500	364000	367726	1904000	1913000	1916581
1-2	370900	377000	377694	2274900	2290000	2294275
2-3	381200	387500	386103	2656100	2677500	2680378
3-4	380900	386500	387815	3037000	3064000	3068190
4-5	382600	384000	387229	3419600	3448000	3455419
5-6	385510	388000	389052	3805110	3836000	3844471
6-7	391250	388000	392161	4196360	4224000	4236632
7-8	395000	391000	394654	4591360	4615000	4631286
8-9	394500	392000	392416	4985860	5007000	5023702
9-10	397500	398000	392245	5383360	5405000	5415947
10-11	387000	383000	385383	5770360	5788000	5801330
11-12	388000	387000	387104	6158360	6175000	6188434
12-1	378000	373000	386983	6536360	6548000	6575417
1-2	439500	436000	435416	6975860	6984000	7010833
2-3	447000	446000	445945	7422860	7430000	7456778
3-4	463000	459000	465896	7885860	7889000	7922674
4-5	465000	464000	467240	8350860	8353000	8389914
5-6	407500	411000	394886	8758360	8764000	8784800

After this test a 45-day run was made under service conditions. Readings from the integrating wattmeter were taken every three hours, the other readings

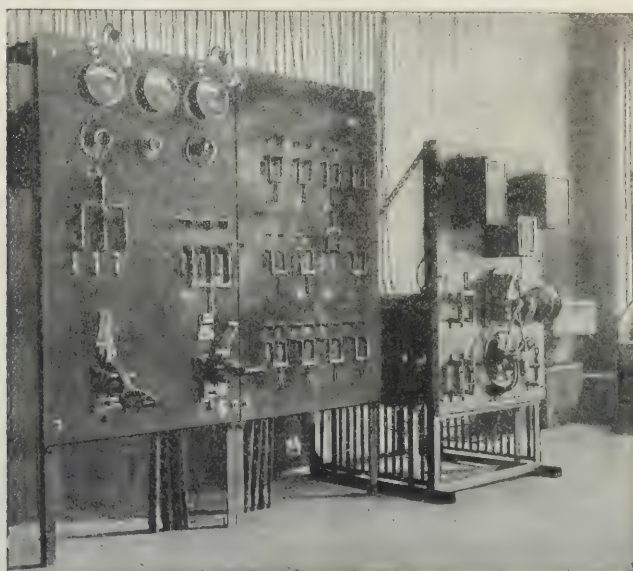


Fig. 8.—Switchboard for meter shown in Fig. 7. Thomas meter board to the right of the station lighting switchboard.

as before. Below is given a log sheet covering a 24-hour period of the test.

24 HOUR LOG OF TEST OF THOMAS METEER BEAVER, PA. NOON, APRIL 26TH TO NOON, APRIL 27TH, 1911

Time	Cu. ft.		Cu. ft. chart	Pressure		Temperature	
	Integrating meter reading.	Integrating meter.		Pitot tube	Brave. Bula.	Brave. Bula.	Bula
12.00	2498.0
3.00	2603.6	1056000	1030800	1056539	134	140	47 46
6.00	2714.3	1107000	1073400	1115176	157	161	47 43
9.00	2831.7	1174000	1134000	1160802	156	160	47 43
12.00	2965.0	1333000	1321200	1311671	162	167	47 43
3.00	3086.7	1217000	1230600	1226774	162	166	47 42
6.00	3215.0	1283000	1302900	1310577	114	124	47 40
9.00	3375.0	1600000	1631400	1614811	113	125	47 40
12.00	3523.2	1482000	1479000	1480000	135	143	47 46

Totals 10252000 10203300 10276350

The flow during the test varied from 90,000 to 640,000 cubic feet per hour, the pressure from 45 to 185 pounds gauge and the temperature between 45 degrees and 65 degrees F. The slight variations in readings between the two meters can be accounted for by the distance between them, these errors averaging out for long periods. A summary of the test shows these results:

22-Hour test, April 9th and 10th, 1911: Total standard cubic feet of gas by Pitot tube for 22 hours, 8,784,800; total standard cubic feet of gas by electric meter for 22 hours, 8,764,000.

$$\frac{8,784,800 - 8,764,000}{8,784,800} = 0.2 \text{ per cent. difference.}$$

Service test, April 17th to June 3rd, 1911: Total standard cubic feet of gas by Pitot tube, 337,546,182; total standard cubic feet of gas by electric meter, 336,732,018.

$$\frac{337,546,182 - 336,732,018}{337,546,182} = 0.02 \text{ per cent. difference}$$

After the test an analysis of the gas gave a composition quite different from that assumed for the design, but its specific heat was nearly identical with the specific heat assumed. An inspection afterward showed the meter in perfect running condition.

These tests show conclusively that the theoretical grounds on which the meter design is based are correct; that the meter will operate satisfactorily on air, artificial gas and natural gas with widely fluctuating temperatures, pressures and gas composition giving readings directly in standard cubic feet; that the accuracy of the meter is maintained for extended periods of time. With the further advantages of ease of checking for error, small space occupied even for large capacities, small maintenance cost and freedom from clogging with dirty gas, this meter gives an extremely satisfactory instrument for both experimental and commercial use.

LABORATORY OF THE
CUTLER-HAMMER COMPANY,
MILWAUKEE.

DESIGN OF A 30-TON INDUCTION ELECTRIC FURNACE.¹

By ALBERT HJORTH.

Received Sept. 23, 1911.

The design of this furnace has been based upon the data and results obtained with the original 5-ton

¹ Presented at the twentieth general meeting of the American Electrochemical Society, in Toronto, Canada, September 21-23, 1911.

furnace in Jossingfjord, Norway, as shown in the daily report sheets.

As the step from 5 tons to 30 tons is a rather large one, it was necessary to carefully study beforehand the different factors determining the design. The two most important things to be determined were the power-factor, and the energy required to keep the charge at the working temperature.

The power-factor depends almost exclusively upon the design of the furnace and the periodicity of the supply. With a given resistance in the bath, a certain current is necessary to produce the required temperature. As the bath consists of only one turn round the magnet, the secondary current is equal to the primary current multiplied by the number of primary turns per leg.

The voltage required to pass this requisite current through the primary winding may be divided into two component parts, *viz.*, one required to overcome the ohmic resistance ("The Resistance"), and the other required to overcome the inductive resistance ("The Inductance").

These two factors determine the power-factor of the furnace. With a given inductance the power-factor increases together with the resistance, and with a given resistance the power-factor decreases as the inductance increases.

The total resistance may again be divided into three parts: First, the primary resistance which represents the loss in the primary coils; second, a very small part representing the loss in the iron-core; third, the secondary resistance representing the resistance of the bath, and which may be termed the useful resistance.

This useful resistance depends upon the following three factors: The conductivity of the iron at the working temperature of the furnace; the skin effect; the dimensions of the bath. The first of these factors will be dealt with later; the second, the skin effect, can be neglected for our purpose, as it may safely be assumed that its effect upon the total resistance will be the same, even if the sectional area of the bath is altered considerably.

The third factor, the dimensions of the bath, is of course, the main one. If the skin effect is neglected, the resistance increases proportionally with the length of the bath, and decreases proportionally with the sectional area.

With a given periodicity the inductance depends upon two factors: First, the magnetic resistance, *viz.*, the "reluctance" of the iron-core; second, the magnetic leakage between the primary windings and the bath.

The first of these may be neglected, as the magnetizing current of the furnace without any charge is only very small.

The second one, the magnetic leakage, depends upon the total flux which passes round any one of the windings (the primary winding and the bath) without also passing round the other; in other words, upon the total flux which escapes through the annular spaces between the two windings.

If the radial width of both the bath and the primary coils remains the same, this flux is practically proportional to the total area of the space between the

The weight of the core is approximately 15 tons. The periodicity of the supply is 12.5 complete periods, corresponding to 25 alternations per second.

From the daily report sheets recording volts, amperes and kilowatts, taken at intervals of about half an hour and extending from the beginning of July until the middle of October, 1910, we have selected six at random, and from these plotted diagrams showing the readings as ordinates, with the time as abscissas. Three of these diagrams are shown in Figs. 2-4. These are for the charges No. 45 (which was the charge witnessed by Professor Jos. W. Richards¹), No. 50 and No. 63. During the first two, pig iron was melted and converted into steel, whereas the last one was run for the purpose of refining low-grade steel.

In scrutinizing these curves, it will be found that the electrical conditions have varied considerably, and in fact, more so than one is accustomed to expect in an induction furnace. This is partly due to the fact that the curves are plotted from actual readings on indicating instruments instead of being traced by recording instruments. In this way the peaks in the curves are naturally more pointed than

would otherwise have been the case, and partly caused by the voltage of the generator being varied a good deal in order to alter the temperature of the bath.

Some of the peaks are evidently caused by the

winding and the bath, and if the distance between these two be not altered, the flux is proportional to the circumference of the bath.

Consequently the inductance will increase with the diameter of the coils; if at the same time the radial width of the bath be increased, the inductance will be somewhat reduced again, but not nearly proportional to the increase in the width.

The inductance is also, of course, proportional to the periodicity, and may be lowered by using a lower periodicity. The influence of this will be more fully discussed later on.

The design of the present furnace is shown in Fig. 1. The data for the furnace are the following:

Mean diameter of the annular space occupied by the bath, 2.1 meters.

Width of this space, 20 cm.

Depth of the bath with a 5-ton charge, 27 cm. (specific gravity of the iron assumed to be 7).

The primary coils have 15 turns on each leg, 8 below and 7 above the bath. Each turn has a sectional area of approximately 1,000 sq. mm. The resistance of each leg at a temperature of approximately 180° C. is 0.003 ohm.

The weight of copper per leg, 840 kg.

The core is approximately 40 by 50 cm., giving an effective sectional area of 1,800 sq. cm.

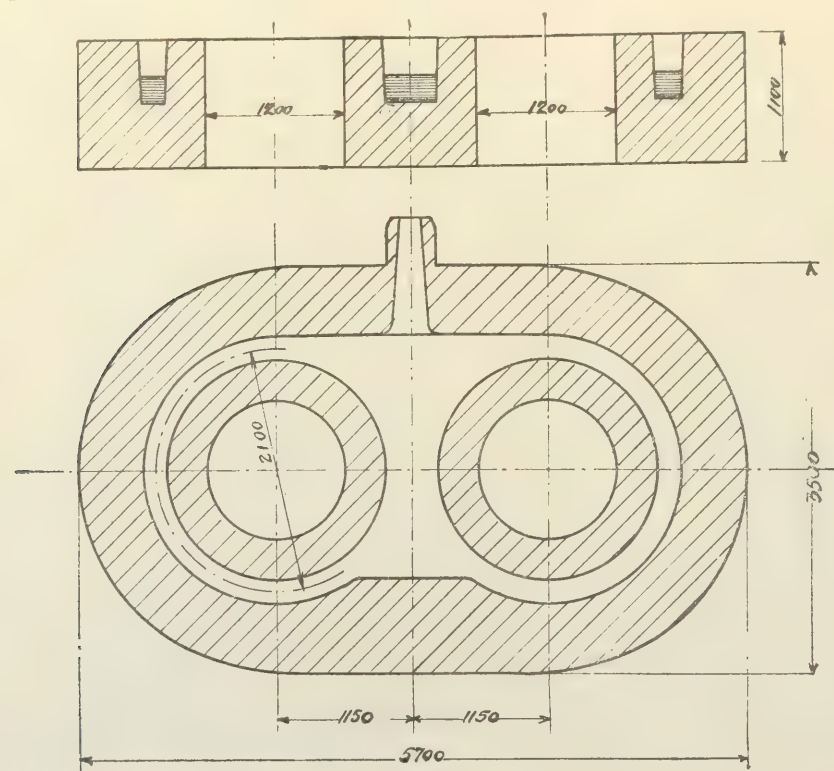
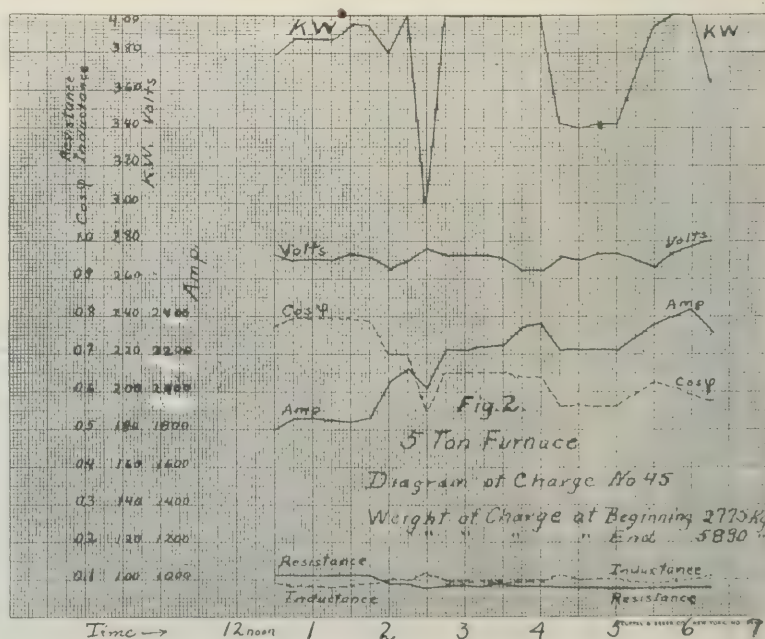


Fig. 1.



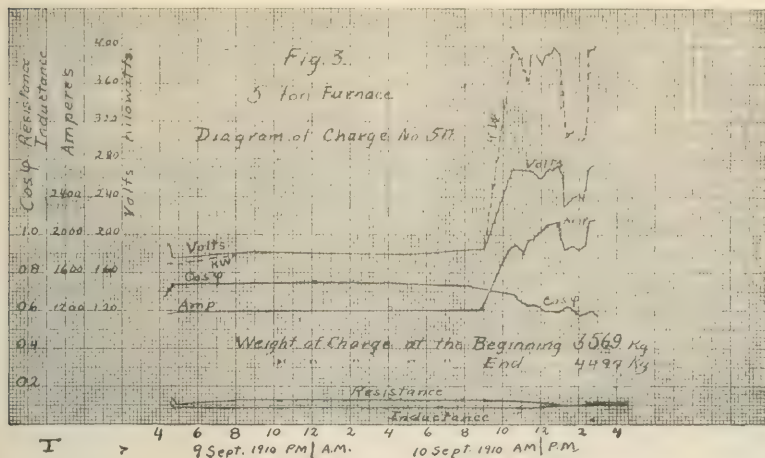
lifting of the upper primary coils in order to gain access to the bath, either for inspecting purposes or in order to work the slag or to add material to the bath. An

¹ These Transactions, 18, 200 (1910).

example of this last-named disturbance is shown very clearly at 2.30 P.M. during charge No. 45. In this case the voltage has been kept constant and the inductance has been suddenly increased, due to the lifting of the upper coils. This causes a drop in the drop amperage, the power-factor and the energy, although the voltage was not altered. These diagrams also

abnormally low, it is safer to assume that the readings, being at the lower part of the scale, are somewhat inaccurate.

If we consider only the resistance at the end of a run or at the beginning, before fresh material is added, we obtain the following figures for the resistance from the reports analyzed:



Charge No.	Weight, kg.	Sectional area, sq. cm.	Total resistance, Ohm.	Equivalent useful resistance, Ohm.
8	1475	160	0.390	0.380
8	5032	545	0.094	0.086
29	2532	273	0.128	0.120
29	5878	635	0.066	0.058
41	3600	390	0.124	0.116
41	5764	623	0.070	0.062
45	2775	300	0.125	0.117
45	5890	630	0.070	0.062
50	3569	386	0.125	0.117
50	4497	485	0.088	0.080
63	2905	314	0.140	0.132

The last column in this table gives the equivalent useful resistance, viz., the total resistance of the bath (twice the resistance of one ring) multiplied by the square of the number of primary turns.

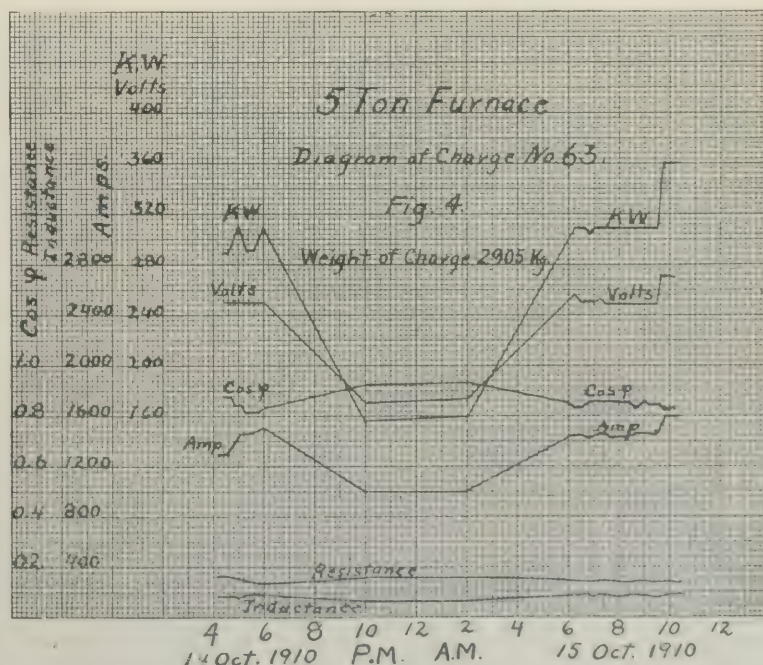
show the variations in the power-factor, the resistance and the inductance. These last named have been arrived at by splitting the voltage up into its two component parts, as explained on page 849, and dividing these by the current. The results thus obtained represent directly the resistance and the inductance, as defined on page 849.

As has already been explained, the resistance and (with a given periodicity) the inductance are constants which depend upon the dimensions of the bath, the weight of the charge (which depends upon the sectional area of the bath) and upon the disposition of the primary coils relative to the bath.

Considering the resistance first, this should, in accordance with the above theory, remain the same as long as the weight of the charge is the same. Apart from the variations caused by the adding of fresh material to the bath, there is, however, a marked decrease of the resistance as the process progresses; whether this is due to the alterations in the chemical composition, or whether the conductivity, after a certain temperature has been reached, begins to increase again with a further increase of temperature cannot be stated definitely without further investigations.

This decrease of the resistance in the course of the run is shown very clearly on the diagram (Fig. 2) and also toward the end of the diagram (Fig. 3). In Fig. 4 this phenomenon is not observed, perhaps because this charge was only for refining purposes. It appears from the diagram as if the resistance was somewhat higher during the night, when the temperature was lower, but as the inductance at the same time appears

In order to obtain this equivalent useful resistance, the total resistance has to be reduced by an amount corresponding to the resistance of the primary coils and to the losses in the iron-core. As stated already, the resistance of the primary coils is 0.003 per leg = 0.006 for the whole furnace. The iron losses may be taken to represent the resistance equal to 0.002,

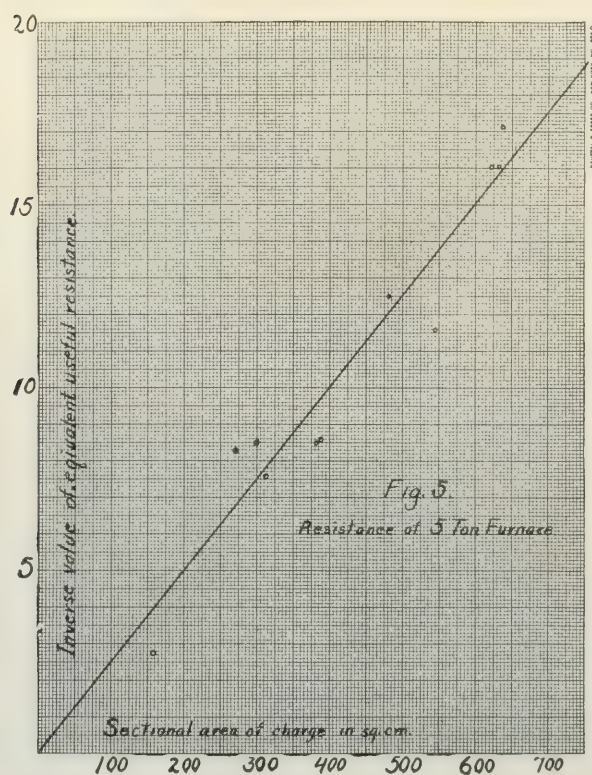


corresponding to an iron loss of approximately 1-2 per cent., and the total of these will thus be 0.008. Subtracting these figures from the total resistance, we obtain the equivalent useful resistance given in the last column.

As the resistance varies in inverse proportion to the sectional area, the curve showing the relation between

the sectional area and the inverse value of the resistance should be a straight line. In the diagram (Fig. 5) the points obtained are marked as dots, and the straight line drawn so as to represent the average of the readings.

In figuring the actual resistance from this curve, one obtains a specific resistance of the molten iron equal to 1.4 ohms per sq. mm. cross-section and m. length. In handbooks the value given is somewhat higher, and even as high as 1.7. The discrepancy may be due to inaccuracies, which are quite unavoidable, considering the difficult nature of the measurements, or may be due to the fact that in our case the section of the bath is not absolutely uniform and that, for instance, the central portion of the bath, where the two rings meet, represents a somewhat lower equivalent resistance than the rest. The value



1.40, it must be remembered, includes all the irregularities in the shape of the bath, and also the skin effect, as far as this influences the resistance. It can only be used for figuring the resistance of furnaces of similar shape and disposition of the bath.

As mentioned on page 849, the inductance is independent of the weight of the charge, and remains constant at all times. It will be seen from the diagrams presented that the inductance varies between 0.09 and 0.10, except when the upper coil is lifted, and during the night (as in case of charge No. 63); but as the readings in this case, as already pointed out, are probably inaccurate, we may neglect this part of the diagram. All the other diagrams correspond to those shown, and the value of the inductance for the old furnace may therefore be taken as 0.095.

Using the figures thus established for the resistance and the inductance, we can figure out theoretically

the power-factor of the present furnace with different charges, and obtain the following table:

With 3 tons Cos. φ	= 0.81
With 4 tons Cos.	= 0.73
With 5 tons Cos.	= 0.65
With 6 tons Cos.	= 0.60

As will be seen, this corresponds very well with the values given on the curves representing the different charges.

We are now in possession of the necessary figures to proceed with the design of the large furnace and to base it upon the experience with the old one.

With regard to this design, the first condition, of course, is that the space for the charge must be large enough to hold 30 tons, but the actual dimensions and shape of the bath must be such as to give the best possible power-factor.

In order to increase the capacity of the furnace, it is necessary to increase the sectional area of the bath more than the length, as otherwise the diameter of the bath, and consequently the dimensions of the furnace, would become too large. The resistance of the bath will thus be considerably decreased, and at the same time the inductance will be increased, owing to the larger diameter which increases the area of the space between the primary and the secondary windings.

The power-factor will thus in any case be reduced with the increased capacity, and we have figured that a 30-ton furnace built on the same line as the present one, for single-phase current, with a two-leg magnet and a current supply with 25 alternations, would show a power-factor equal to 0.25, and that the power-factor even with 15 alternations per second would still be only 0.38.

It was therefore decided by me that the 30-ton furnace should be built on the three-phase principle instead of the single-phase. In this case the weight of the charge per ring in only 10 tons instead of 15 tons with a single-phase furnace, and, as will be shown later, the reduction of the power-factor is not nearly so great.

In order to facilitate the tilting of the furnace, the three rings were disposed in one row. This arrangement is not strictly symmetrical, and it is to be expected that the load on the middle phase will be somewhat different from the load on the two outer ones, on account of the difference both in the inductance and in the resistance. With a special supply this is, however, not a very serious drawback, particularly as the difference between the phases in all probability will not be very great.

The dimensions finally chosen for the new furnace are shown in Fig. 6; from this we may now determine the resistance and the inductance in order to arrive at the power-factor.

Using the figure 1.40, the useful resistance figures out to be approximately 0.0001.

In order to arrive at the total resistance, this has to be increased approximately 7-10 per cent. on account of the losses in the primary winding and the iron-core, and the total equivalent resistance based on one winding becomes then 0.00011.

The inductance of the old furnace was 0.095, or, reduced, to one turn, 0.00021. In the new furnace this will be increased in proportion to the diameter, that is, $\frac{0.00021 \times 3}{2.1} = 0.0003$.

These values of the resistance and the inductance would give a power-factor equal to 0.34, which is still too slow.

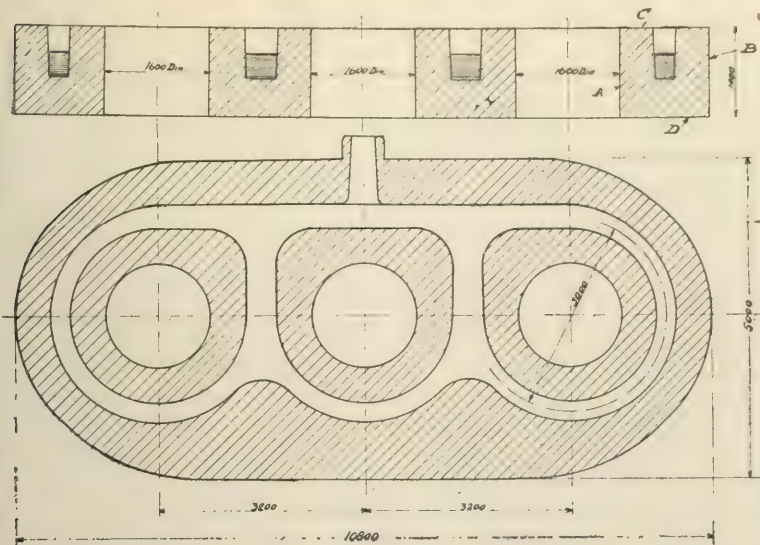


Fig. 6.

In order to increase the power-factor, it is necessary to further decrease the inductance by using a lower periodicity. What can be obtained in this way is shown in the following table:

Periodicity.	Power-factor.
25 alts.	0.34
20 alts.	0.41
16 alts.	0.50
10 alts.	0.67

From this table we select a periodicity of 16 alternations per second. To decrease the periodicity further still will hardly pay, seeing that the cost of the generator will thus be further increased, even if the output is reduced on account of the power-factor being improved. This, however, is a matter which should be gone into more closely later on, in connection with the actual cost of the generator.

It remains to figure out the necessary energy required for the furnace, the dimensions of the iron-core and the number of primary turns, together with the sectional area of these.

As the furnace will be used with a liquid charge, and no melting-down will take place, the amount of energy required is only the amount necessary to keep the bath at the required temperature. Apart from the small losses in the primary coil and the iron-core, all the energy is converted into heat in the charge itself, and, as soon as a constant temperature is reached, finally conducted to the surface of the furnace and given out from this by radiation, conduction and through the cooling arrange-

ments. If the water-cooling is arranged in the same way and the amount of water increased correspondingly, it may therefore be assumed that the loss of heat, and consequently the energy required to keep the charge hot, will be in proportion to the surface of the furnace.

From Fig. 6 we determine the surfaces of the old and new furnace, as follows:

	New furnace	Old furnace.
Inside circular surface (A)	20.5 sq. m.	8 sq. m.
Outside surface (B)	35.9 sq. m.	17 sq. m.
Upper surface (C)	28.0 sq. m.	15 sq. m.
Lower surface (D)	28.0 sq. m.	15 sq. m.

The surface of the new furnace is consequently between two and two and a half times as large as the old one. The amount of energy required in the old one to keep the charge in a molten condition during the night was approximately 180 kw., and during the refining energy varied between 250 kw. and 350 kw. The minimum energy required for the new furnace should consequently be $2 \times 180 = 360$, and the maximum, $2.5 \times 350 = 875$. We have assumed 700 kw., but at the same time the generator should be constructed in such a way that, by merely altering the voltage, it can give anything between 400 and 1,000 kw. With 700 kw. the current per ring becomes approximately 46,000 amperes, and

the current density in the bath will be about 0.34 ampere per sq. mm.

The further data of the furnace, based upon the figures arrived at above, are:

Iron-core, 1,200 sq. cm. Weight, about 23 tons.

Primary windings; voltage, 230 volts.

Number of turns per leg, 13: disposed 7 below the bath and 6 above.

Sectional area, 2×20 cm.

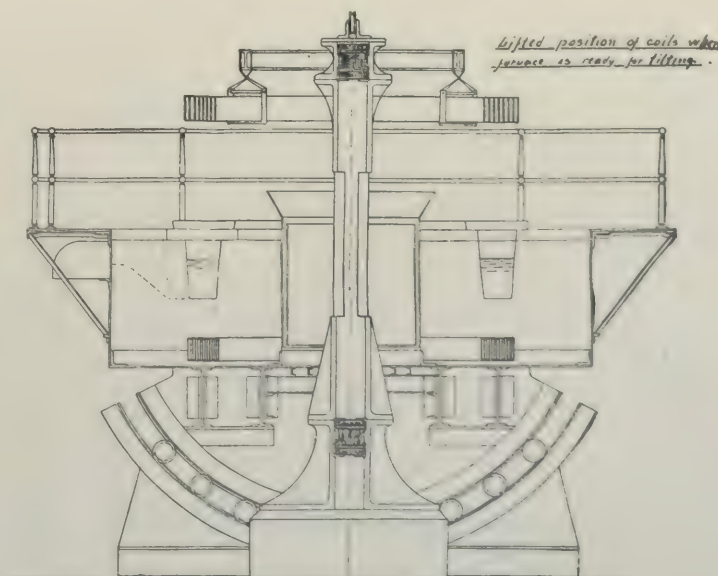


Fig. 7.

Weight of copper for the whole furnace, about 13.5 tons.

As stated above, the theoretical number of turns is only 13, but in order to be able to run the furnace

The lower coil is embedded in the masonry below the bath, and consists of copper tubes arranged for water-cooling. The upper coil may be lifted in order to inspect the bath.

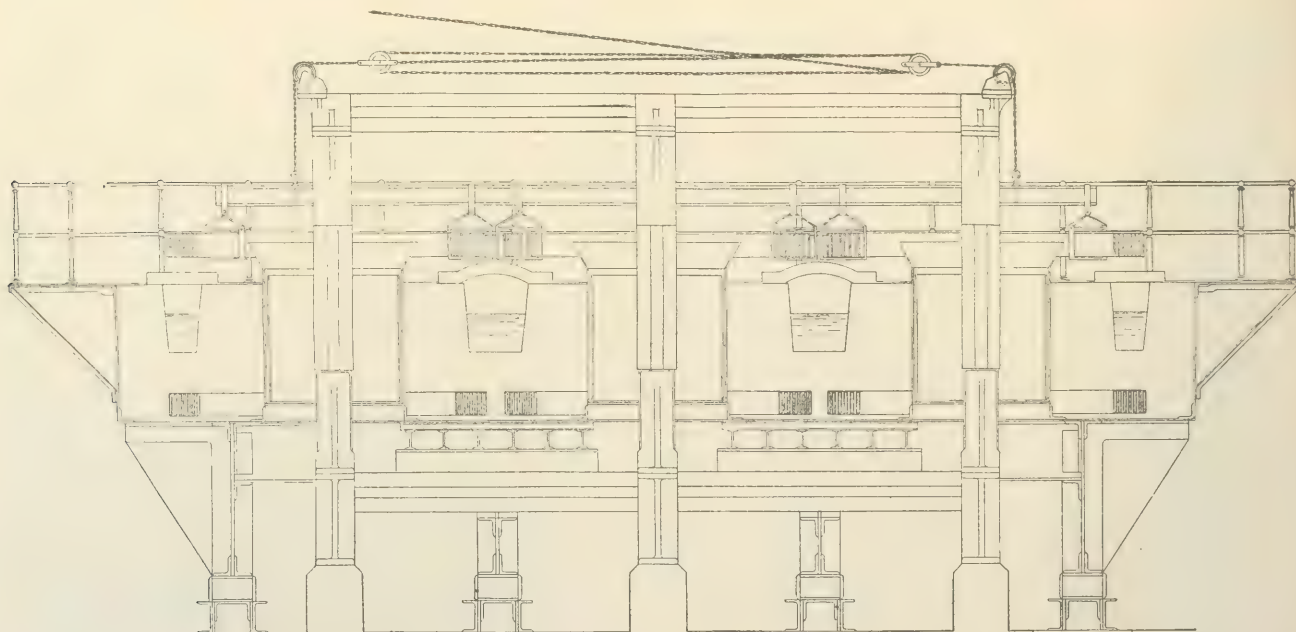


Fig. 8.

at full charge, even if the inductance and resistance should prove to be somewhat different from the values given, two turns should be added per leg, making the number of turns in the upper coils 8. The last

The inner surface of the furnace, marked "A" on Fig. 6, is also arranged for water-cooling.

In order to keep the covers for the bath small, the channels were given the form shown in Figs. 6, 7, 8

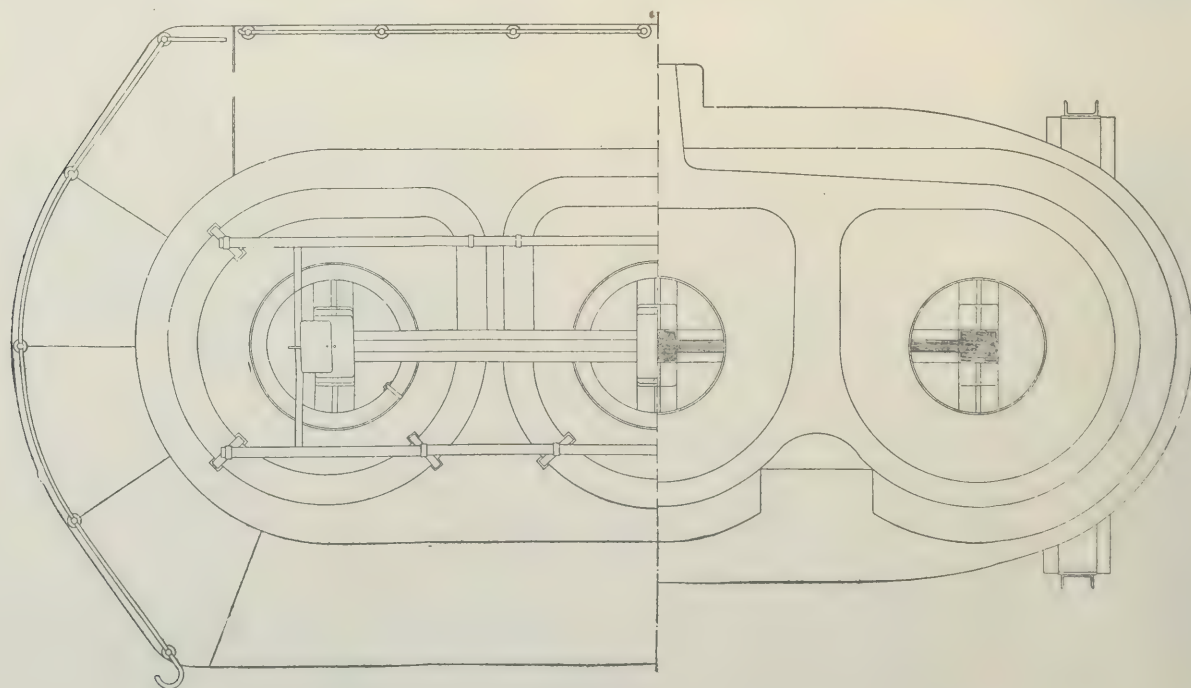


Fig. 9.

three turns in each of these coils should be provided with terminals, enabling one to use at will 12, 13, 14 or 15 turns per leg.

In Figs. 7, 8 and 9 is shown a general arrangement of this furnace, designed on the same lines as the old one.

and 9. The primary coils have been shaped accordingly to follow the shape of the bath as closely as possible.

The primary voltage has been fixed at about 230 volts, as this low voltage greatly facilitates the construction and the insulation of the windings. To

embed the coil in the masonry of the furnace would, for instance, be impossible with a higher voltage, and also the upper coil would have to be built and cooled in quite a different manner if it had to carry high-tension current. The use of high-tension current

The generator should, according to the foregoing, be designed for a normal output of 700 kw., 8 periods (corresponding to 16 alternations) per second, 230 volts, 3,540 amperes, and a power-factor of 0.5. At the same time it must be able to give 400 kw. at 165

Table showing Electrical Conditions of 30-Tons Furnace
with varying Resistance and Inductance

No	Variations in		1 Min. 2 Norm. 3 Max.			Cos ϕ	Remarks.	
	Resistance	Inductance	No.	K ² W	Volts			Amper.
1	± 0	± 0	1	468	175	2700	0.5	
			2	760	275	3540		
			3	1000	275	4200		
2	+25%	± 0	1	432	175	2400	0.58	The charge may be increased to 375 tons without reducing the power-factor more than 10%. The max and min energy as well as current and voltage will then be the same as in the first case.
			2	760	275	3160		
			3	1000	275	3860		
3	-25%	± 0	1	544	175	2860	0.40	If the charge is reduced to 225 tons, the power-factor will be .5 and the conditions again the same as in the first case.
			2	760	275	3650		
			3	775	275	4200		
4	± 0	+25%	1	288	175	2275	0.42	If the number of turns is reduced to 12 and the charge at the same time reduced to 24 tons, the power-factor will be .5, and the max. Energy 950 K ² W at 275 volts. Accordingly.
			2	760	275	3540		
			3	710	275	3570		
5	+25%	+25%	1	325	175	2170	0.5	By reducing the number of primary turns to 12, the max. Energy may be increased to 950 at 275 volts, 4000 amp. Power-factor .5
			2	760	275	3160		
			3	815	275	3420		
6	-25%	+25%	1	234	175	2370	0.325	If the charge is reduced to 18 tons and the number of turns at the same time reduced to 12, the max. Energy will be 950 K ² W at 275 volts, 4000 amp. Power-factor .5
			2					
			3	578	275	3125		
7	± 0	-25%	1	611	175	3210	0.61	By increasing the number of turns to 15, the charge may be increased to 40 tons. The electrical conditions will then be as in the first case.
			2	760	275	3540		
			3	1000	275	4200		
8	+25	-25%	1	628	175	3000	0.69	By increasing the number of turns to 15, the charge may be increased to 50 tons. The electrical conditions will then be as in the first case.
			2	760	275	3160		
			3	1000	275	3800		
9.	-25	-25	1	550	175	3630	0.5	By increasing the number of turns to 15, the max. Energy will be 1000 K ² W and the conditions otherwise the same as in the first case.
			2	760	275	4050		
			3	770	275	4300		

Fig. 10.

would therefore necessitate a considerably increased distance between the bath and the coils, and thus a considerably lower power-factor.

The table below shows the principal data for the old furnace and the new one:

	Old furnace.	New furnace.
Total capacity.....	5 tons	30 tons
Capacity per leg.....	2.5 tons	10 tons
Diameter of bath.....	2.1 m.	3 m.
Width of bath.....	20 cm.	30 cm.
Depth of bath.....	27 cm.	45 cm.
Total surface of masonry.....	55 sq. m.	110 sq. m.
Total length of platform.....	8 1/4 m.	13 m.
Total width of platform.....	5 1/4 m.	6.5 m.
Sectional area of core per leg.....	1800 sq. cm.	1200 sq. cm.
Weight of core.....	15 tons	23 tons
Number of primary turns per leg.....	15	13
Sectional area of primary windings....	1000 sq. mm.	4000 sq. mm.
Weight of copper per leg.....	0.875 tons	ca. 4.5 tons
Total weight of copper.....	1.75 tons	ca. 13.5 tons
Energy used.....	250 kw.	700 kw.
Copper losses.....	12.3 kw.	40 kw.
Iron losses.....	18 kw.	18 kw.
Power factor.....	0.65	0.50
Voltage.....	250	230
Periodicity (1/2 alterations per second)	12 1/2	8
Amperes per phase.....	1400	3540
Kind of current.....	1 phase	3 phase

volts, and 1,000 kw. at 275 volts, with the same power-factor, and 290 and 125 kw., respectively, with a power-factor of 0.362. The maximum current will thus be 4,300 amperes.

The engine or turbine driving this generator should be for a maximum output of 1,550 effective h. p., and run at a practically constant speed at all loads between 600 h. p. and 1,550 h. p.

This plant should be quite sufficient to supply energy to the 30-ton furnace, even if the constants of this should vary considerably from the figures given above. In order to study this, we have prepared the table (Fig. 10) showing what would happen, and the maximum and minimum energy which could be supplied to the furnace, in case either the resistance or the inductance, or both should vary 25 per cent. from the assumed value, either up or down.

This table shows the reason why the upper coils should be provided with connections, such as heretofore described, as these coils enable one to compensate for quite considerable variations, both in the resistance and in the inductance.

KRISTIANIA, NORWAY.

ADDRESSES.

(Concluded from the October No.)

SOME PROBLEMS IN CHEMICAL ENGINEERING PRACTICE.¹

By F. W. FRERICHS.

THE CLASSEN LIGNUM CO.

On April 18, 1903, there was submitted to me a circular issued by bankers in New York, Chicago and St. Louis, offering 5,000 shares of 7 per cent. cumulative preferred stock of the Classen Lignum Co. at par, each share of preferred stock to receive one share of common stock as a bonus.

The total capitalization of the company was \$2,500,000, divided into \$600,000 of 7 per cent. cumulative preferred stock and \$1,900,000 of common stock.

Everything was in readiness to put the stock on the market, but before doing so the bankers submitted to me a full typewritten statement of forty pages, setting forth the nature of the process as described by the inventor, and a number of reports on its working, made by chemists of reputation, on the strength of which subscriptions were to be solicited on the stock-market five days hence.

I was requested to make a final comment on the proposition and complied with this request two days later, on April 20, 1903.

Dr. A. Classen, of Aachen, Germany, described his process as follows: The object of the process was to turn sawdust into valuable products, and the Classen Lignum Co. proposed to work the large accumulations of sawdust in the northwestern lumber districts of the United States. The Classen process utilizes the action of sulphurous acid upon wood, which is a dissolving action without converting it into glucose. Subsequently, the surplus acid is oxidized to sulphuric acid by the oxygen of the air, and the sulphuric acid thus produced converts the soluble cellulose into glucose of a quality which is readily converted into alcohol by fermentation.

The insoluble part of the sawdust, which is called the tailings and consists of about three-quarters of the original weight of the sawdust used, is pressed into briquettes, from which, by dry distillation, wood tar, methylic alcohol, acetone, acetate lime, and charcoal are obtained, and as an important feature of the process, it was taken into account that the products from the tailings would not only pay the cost of the sawdust and of the entire Classen process, but would moreover yield a fair profit by themselves. The calculation of cost and probable profits of these by-products was among the papers submitted to me. To this I shall refer later on.

In two experimental plants at Aachen and Chicago, the alcohol part of the process was tested by experiments of many months' duration. It was proven that the product was really alcohol, but no figures were given which could prove anything about its cost. By guess work the conclusion was reached that the

manufacture of alcohol from sawdust would not cost more than the manufacture of alcohol from grain.

This conclusion seemed entirely satisfactory since the calculation of the by-products was showing for itself a large profit, and was expected to carry the process to a successful end. Full reliance was placed upon the judgment of the men who had conducted the tests, and to secure public confidence in the proposition, the full titles and honors of those engaged in the investigation were given for the purpose of characterizing the men, who were recommending subscription to stock in the company.

In such condition the reports came to me. There was no time to repeat experiments since the paper was ready to be put on the market. Moreover was it likely that the experiments were correctly conducted since chemists of good reputation had signed their name to the reports, but some of these chemists were men of science and for this reason the calculations seemed to require my attention.

The only calculation in the report was for the by-products and it was made for European conditions. It had not occurred to any one of the investigators that the same calculations might not apply to an American plant. I made a calculation for American conditions, based upon the same figures for weights and quantity, time and materials, which were used in the European calculation by constructing the table given below, in which is seen a comparison of the rentability of the process in Europe and in the United States.

This table (Table I) I submitted with the following comment:

Line 1.—The price of 4 Pf. per kilogram, or 10 cents per bushel of charcoal may be right for Europe, but is entirely too high for the United States. I was buying at that time single car-load lots at 6 cents per bushel, f. o. b. place of production, and since it was proposed by the Classen Lignum Co. to use the charcoal for blast furnaces, even 6 cents would be prohibitive, and it was believed that not more than 4-5 cents could be obtained at that time. Figuring 5 cents would reduce the income for charcoal to one-half.

Line 2.—Calcium acetate, 80-82 per cent., was valued at 1½ cents per lb. This was entirely too high. As a matter of fact, acetate lime at that time was manufactured at a great surplus in the United States and exported to Europe, where it was sold at 1½ cents per lb., but this included the freight from the place of production to European markets and included also the profits of a firm in New York, which had monopolized the article, so that the manufacturer in Michigan at that time received less than 1 cent per lb. for his product. As a matter of fact, the price of acetate lime, 74 per cent., f. o. b. place of production in Michigan, had not been higher than 0.8 cents for ten years. This caused another shortage in the receipts of the proposed works.

Line 3.—It is true that the nominal value of wood spirits in the United States at that time was 65 cents per

¹ Address delivered at the semi-annual meeting of the American Institute of Chemical Engineers, June 21, 1911.

gallon, but the price actually received by the manufacturer was much less, since the American market at that time did not absorb more than half of the production. The price for the whole consumption was kept up artificially by an American syndicate and the surplus was exported to foreign markets. In my opinion, not more than 50 cents per gallon could be obtained, which makes another reduction in the receipts of the proposed works.

Line 4.—1250 kilograms of pine tar were valued at 125 M. While pine tar in Germany may have this value, it has in this country no value at all. In

and an equal amount for general expenses, bookkeeping, stationary, postage, storage, and taxes is none too high.

Line 14.—Lime and other materials are very high in the northern states, and \$2,000 in place of 6,500 M. is very low figuring.

Lines 17 and 18.—The buildings and machinery, the cost of which is estimated at 278,560 M. under European conditions, cannot be erected in the United States for less than \$125,000 and 10 per cent devaluation on this amount will add \$12,500 per year to the expense account. To run the works, at least \$25,000

TABLE I.

Estimate of prospective profits on working 25 tons tailings a day from Classen's Alcohol Process by Heidenstom's patent.

RECEIPTS

For Europe.

For the United States

Marks.

Marks.

Dollars.

Dollars.

1.....	Charcoal.....	12,000	kilograms..	0.04	480.00
1.....	Charcoal.....	1,200	bushels....	0.05	60 00
2.....	Calcium acetate 80/82..	575	kilograms..	0.15	86 25
2.....	Calcium acetate 80/82..	1,265	pounds....	0 01	12 65
3.....	Wood alcohol.....	87.5	kilograms..	0.70	61.25
3.....	Wood alcohol.....	28	gallons....	0.50	14 00
4.....	Pine tar.....	1,250	kilograms..	0.10	125 00
4.....	Pine tar.....	1,250	kilograms..	0 00	..
5.....	Total per day.....	752.50	..	86 65
6.....	For 300 working days.....	M. 225,750.00	..	\$25,995 00
EXPENDITURES.							
7.....	25 tons sawdust.....	2.00	50 00
7.....	25 tons sawdust.....	0 50	12 50
8.....	15 tons sawdust, for fuel.....	2.00	30 00
8.....	15 tons sawdust, for fuel.....	0 50	7 50
9.....	40 shifts' wages of 12 hours each.....	3.00	120 00
9.....	40 shifts' wages of 12 hours each.....	1 50	60 00
10.....	Total per day.....	M. 200.00	..	\$ 80.00
11.....	For 300 working days.....	M. 60,000.00	..	\$24,000.00
12.....	Superintendent per year.....	2,000.00	..	2,000 00
13.....	Expenses, taxes, insurance, storing.....	15,000.00	..	7,500.00
14.....	Lime and sundry materials.....	6,500.00	..	2,000.00
15.....	Sundries and repairs.....	10,000.00	..	2,500.00
16.....	Patent license.....	10,000.00	..	2,500.00
17.....	Devaluation on machinery and buildings.....
	10% on M. 278,500.....	27,850.00
18.....	Do. 10% on \$125,000.....	12,500 00
19.....	Interest, 5% on M. 320,000.....	16,000.00
20.....	Interest, 5% on \$150,000.....	7,500 00
21.....	Total expenditures.....	M. 147,350.00	..	\$60,500.00
22.....	Total receipts.....	M. 225,750.00	..	\$25,995 00
23.....	Profit.....	M. 78,400.00	Loss.....	\$34,505.00

Europe it is used for painting sheds and cheap buildings, but in the United States nobody would think of using pine tar for this purpose. The odor imparted to the buildings by this paint is of such a character that no American would live in the same. In reality, all the American charcoal works run the pine tar to waste, or use it for fuel, and there is no value to it.

Line 9.—The wages for every twelve-hour shift were figured at 3 M. or 75 cents. This was too low. No laborer in the United States would work twelve hours for less than \$1.50.

Line 12.—The manager who is at the head of works, costing about \$125,000 could not be had for a salary of 2,000 M. or \$500 a year. \$2,000 a year would be a small salary for an efficient man.

Line 13.—The rate of insurance in the lumber district being 3 per cent would amount to \$3,750,

working capital would be necessary, which makes the entire capital used for the plant, \$150,000, the interest of which at the rate of 5 per cent, equal to \$7,500, must go to expense account.

The result of the comparison was that there was to be a probable yearly loss of \$34,505 for an American plant, against a yearly profit of 78,400 M. for a plant of the same description operated in Europe.

This argument made up on the short notice of one day and submitted to the interested parties caused the prompt withdrawal of the entire proposition, rendering valueless the expert examination of many months considered necessary by scientific chemists, and saved a large sum of money to easy investors.

THE PLANT OF THE KENTUCKY SODA ASH CO.

In April, 1892, I was approached by a syndicate of about twelve prominent men of the highest stand-

ing in the City of Louisville, Ky., to assist them in the erection of ammonia soda works. They were desirous of drawing that industry to the neighborhood of their home city, since near Brandenburg, Ky., about forty miles distant from Louisville, salt works had been operated for a long period of years with natural gas as fuel, which was emanating from the salt wells, together with the brine. In their opinion this occurrence of natural resources could be the foundation of a soda ash industry.

They had the capital, had secured detailed information about the ammonia soda process, and had a man among their number, whom they thought capable of serving as a foreman to run the works. Realizing that the ammonia soda process is largely a process of handling ammonia, they came to me as an experienced ammonia maker, to assist them in the construction of the works.

On the Mooreman farm, near Brandenburg, Ky., salt works had been operated for many years. There were two or three wells, which had supplied the works with salt brine and natural gas.

Since the production of salt had been limited, I had some doubts whether the available quantities of brine and gas would justify the erection of a large plant in that locality, and wrote before commencing work on the plant, on May 5, 1892, to the Kentucky Soda Ash Co. as follows:

"I do not believe that it is advisable to start with the soda ash works before you have proven beyond doubt that you have salt and gas of good quality, and that you have plenty of it. Cheap salt and fuel is the great advantage of your enterprise, and before you spend any money on the soda plant you should be perfectly sure of the first part. If you first sink salt wells and find no sufficient supply, you lose only the money for the wells. If you first build the soda works, sink the wells afterwards and find no supply of salt, then all your expenditures will be a clear loss."

To this I received the reply, that they knew their territory and were willing to take the risk. Moreover, they considered the erection of a 10-ton plant in the nature of an experiment, and would erect a very much larger plant on a different site—possibly in the neighborhood of Detroit, Mich., if the supply of raw material should fail. Their principal aim was to demonstrate that they could make soda ash of good quality and at low cost, and they were decided to make the experiment in their locality.

With this understanding I consented to construct a plant for them and in doing so I directed the construction of the apparatus to the minutest detail, going to many expenses, which would be justified, if the plant were to be

only an experimental works as a forerunner to a larger plant.

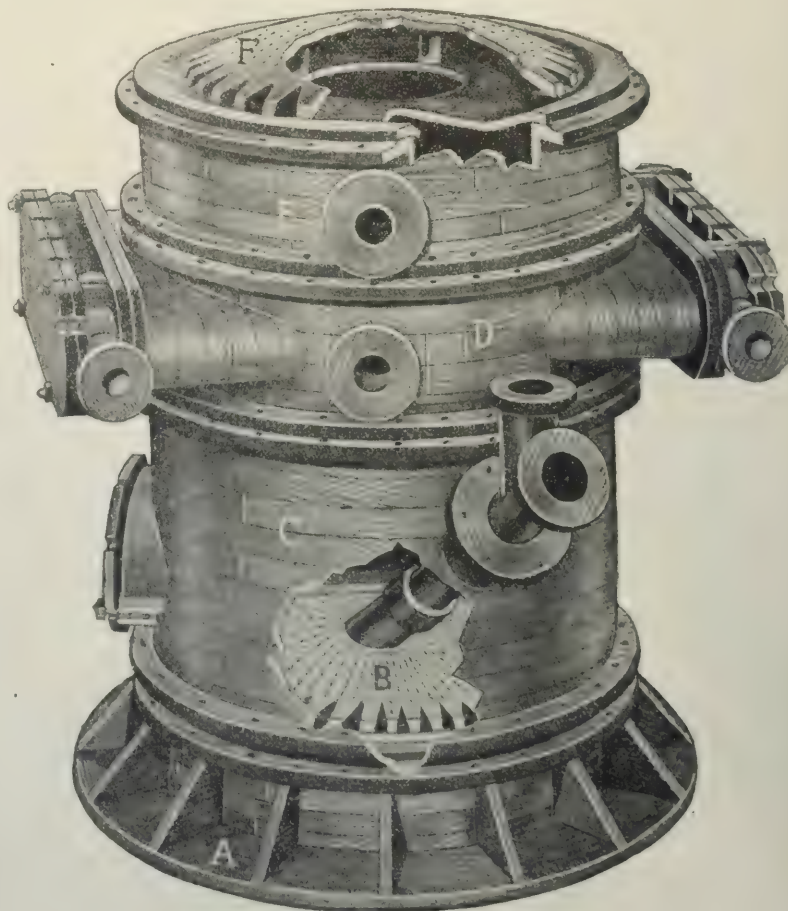
Under these conditions, a plant capable of making ten tons of soda ash per day of 24 hours was erected, and I will state right here, that when completed it started off running without a hitch and in a three months' run demonstrated the successful operation at a low cost. But after three months the salt wells were exhausted and needed a rest of several months before they could be operated again, and it was necessary to shut the works down. In the meantime the financial crisis of 1893 had set in and had swept away the fortunes of some of the stockholders, and the plans for erecting a larger works could not be carried out. So the enterprise came to a termination by the Kentucky Soda Ash Co. going out of business.

Since all of the plans were carried out in great detail they well may serve as an example of going at a problem of chemical engineering, and for this purpose only, I have selected some of the work for presentation in this meeting.

You all know the chemical reactions underlying the ammonia soda process. For this reason it is not necessary to lose time on them.

The apparatus necessary for the process may be divided into the following groups, if brine, limestone and ammonia are given as raw materials:

First.—Lime kilns and carbonic acid washers to make carbonic acid and caustic lime.



Second.—Apparatus for making bicarbonate of soda and converting this into carbonate of soda.

Third.—Apparatus for slaking lime.

Fourth.—Apparatus for recovering ammonia.

Following this introduction a line of 65 lantern slides were projected on the screen with a view of giving one way in which the ammonia soda process might be demonstrated to advanced students in a lecture room. An attempt was made to reproduce these pictures for this publication, but it was found that at the necessary reduction to small size the details in the drawings were lost. For this reason the drawings are omitted and only an enumeration and description of the slides is given in this paper.

The first four slides represented apparatus assembled in the four great divisions of an ammonia soda plant as enumerated above.

Such a division is most desirable in order to facilitate the understanding of the entire and very complicated plant.

Slides Nos. 5-65 gave detail drawings and models of some of the important parts of the plant.

The following list gives a more complete idea of what was offered.

1. Lime kilns and carbonic acid washers to make carbonic acid and caustic lime.
2. Apparatus for making bicarbonate of soda and converting this into carbonate of soda.
3. Apparatus for slaking lime.
4. Apparatus for recovering ammonia.
5. Drawing of lime kiln.
6. Drawing of carbonic acid washer.
7. Drawing of column, general view.
8. Drawing of base of column.
9. Drawing of bottom of column.
10. Drawing of bottom section of column.
11. Drawing of dividing plate of column.
12. Drawing of center section of column.
13. Drawing of cooling section of column, outside view.
14. Drawing of cooling section of column, inside view.
15. Drawing of top section of column.
16. Drawing of cover of column.
17. Drawing of bolts for column.
18. Drawing of gaskets for column.
- 19, 20 and 21. Wooden models representing the parts of the column on the scale of one inch to the foot.
22. Drawing of vacuum filter.
23. Drawing of vacuum filter, displayed.
24. Drawing of roasting apparatus.
25. Detail drawing of same.
26. Top view of same.
27. Detail sheet of machinery on same.
- 28-29. Wooden model of roasting apparatus.
30. Drawing of ammonia still, general view.
31. Drawing of ammonia still, lower half.
32. Drawing of ammonia still, boiler iron work.
34. Drawing of ammonia still, bottom piece.
35. Drawing of ammonia still fittings.
36. Drawing of ammonia still, reducing piece.

37. Drawing of ammonia still, dividing bottom.
38. Drawing of ammonia still, top section.
39. Drawing of ammonia still, dividing bottom.
40. Drawing of ammonia still, cross section same.

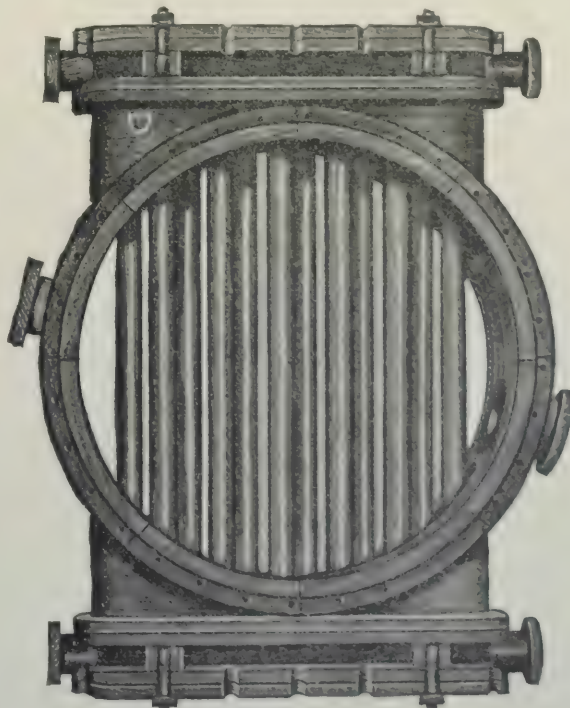
41. Drawing of ammonia still, drip plate.
42. Drawing of ammonia still, cover.
- 43-52. Wooden models made at the scale of one inch to the foot, representing parts of the ammonia still.

- 53-58. Detail drawings of absorbers.

- 59-65. Detail drawings of coolers.



All slides were made from good working drawings from which the actual plant was constructed. In



order to convey the meaning of the drawings more clearly to the pattern makers and to facilitate the arrangement in space of all the apparatus, complete models were made at a scale of one inch to the foot, and as an example 3 pictures of the models for the column are given in the accompanying cuts.

In the experience of the writer such models have been of great service to obtain the construction of chemical apparatus in conformity with drawings, particularly if they had to be made in machine shops where the construction of chemical apparatus is new, or done only at great intervals.

It also is thought that models similar to the ones presented at the meeting are highly instructive for students in chemical engineering. It is true that students even if they are highly advanced in manual training could not make such models themselves, since it takes the best of pattern makers to do that class of work. But it would pay well for any university to have a shop and to employ one or more

pattern-makers steadily to do such work. By so doing they might accumulate in time a stock of models, the manufacture of which will serve to train the instructors, while the models themselves will be a lasting aid in the instruction of students.

Two columns were actually constructed by these drawings and models. Each column was made up of 1 base, A; 1 bottom piece, B; 1 bottom section, C; 17 cooling sections, D, alternating with 16 center sections, E; 35 dividing bottoms, F, cast together with perforated plates, one bottom being located between each pair of sections; 3 top sections, G; and 1 cover H.

The entire finished weight of one column was 177,570 pounds and it was constructed for $3\frac{1}{4}$ cents per pound of machined castings, the price being understood free on board cars at place of manufacture.

Specifications as actually used in construction of the apparatus were accompanying the drawings, and the paper gave a full account of the construction and cost of a ten-ton ammonia soda plant.

SCIENTIFIC SOCIETIES.

REPORT OF COMMITTEE ON STANDARD SPECIFICATIONS.

INDIANAPOLIS MEETING, A. C. S., JUNE, 1911.

The Committee on Standard Specifications, appointed at the meeting of the American Chemical Society held in Boston in 1909 and consisting of Frank G. Stantial, Robert Job and the writer, submits the following report:

As has been noted in previous reports to the Industrial Division, your committee decided that the work could best be carried out by the appointment of a sub-committee for each of the materials selected as the subject of a specification, the personnel of these sub-committees to consist, so far as possible, of three members—two representing the consumers and one the manufacturers. The committee was further of the opinion that inasmuch as other societies were working along similar lines, our efforts should be confined for some time at least to those materials of a strictly chemical nature.

Nine sub-committees were appointed to formulate specifications for the following materials:

Alum,	Soda Ash,
Bleach,	Solder,
Caustic Soda,	Sulphuric Acid,
Muriatic Acid,	Turpentine.
Nitric and Mixed Acids,	

The personnel of these committees is as follows:

Alum.—William M. Booth, Chairman, Syracuse, New York; F. A. Olmsted, Willamette Pulp & Paper Co., Oregon City, Ore.; S. W. Wilder, Merrimac Chemical Co., 33 Broad St., Boston, Mass.

Bleach.—W. P. Atwood, Chairman, Hamilton Mfg. Company, Lowell, Mass.; Fred. W. Farrell, Emerson Laboratory, Springfield, Mass.; Charles E. Acker, 97 Cedar St., New York City.

Caustic Soda.—W. K. Robbins, Chairman, Amoskeag Mills, Manchester, N. H.; James W. Loveland,

Works Manager, B. T. Babbitt, Babbitt, N. J.; J. D. Pennock, Semet-Solvay Co., Syracuse, N. Y.

Muriatic Acid.—Fritz H. Small, Chairman, Graton & Knight Mfg. Co., Worcester, Mass.; J. T. Baker, J. T. Baker Chemical Co., Phillipsburg, N. J.; W. S. Williams, Arthur D. Little, Inc., 93 Broad St., Boston, Mass.

Nitric and Mixed Acids.—Arthur M. Comey, Chairman, E. I. duPont de Nemours Powder Co., Chester, Pa.; Henry U. Walker, Maas & Waldstein Co., Newark, N. J.; Oscar W. Pickering, 42 Holden St., Malden, Mass.

Soda Ash.—Henry W. Hess, Chairman, Libbey Glass Works, Toledo, Ohio; Martin L. Griffin, Emerson Laboratory, Springfield, Mass.; A. F. Shattuck, Solvay Process Company, Detroit, Mich.

Solder.—Carl F. Woods, Chairman, Secretary, Arthur D. Little, Inc., 93 Broad St., Boston, Mass.; W. M. Corse, Lumen Bearing Company, Buffalo, N. Y.; George O. Bassett, Western Electric Company, 463 West St., New York City.

Sulphuric Acid.—Fred B. Porter, Chairman, Chemist Swift Fertilizer Works, Atlanta, Ga.; W. M. Kelsey, Supt. Acid Department, Mineral Point Zinc Co., Depue, Ill.

Turpentine.—J. E. Teeple, Chairman, Hudson Terminal, 50 Church St., New York City; C. H. Herty, University of North Carolina, Chapel Hill, N. C.; L. F. Hawley, U. S. Forest Service, Washington, D. C.

The sub-committees on bleach and solder specifications have completed their work and have submitted the requirements of these respective materials. These have been drafted into a form agreed upon by the main committee and are submitted to the Division for adoption or whatever action may be deemed proper.

Bleach.—The specifications for bleach are, so far as we know, different from any others in use. It

seemed wise, in view of the variable composition of bleaching powder, that some provision be made for purchasing upon a unit basis, in much the same manner as is done in the case of other chemicals.

Solder.—In the case of the solder specifications, no attempt has been made to cover special solders since their composition is necessarily dependent upon their specific uses and the total amount used is small as compared with the more common types. The requirements for fine solder were formerly and are now in many cases 50 per cent. tin and 50 per cent. lead. Careful service tests carried out by a very large consumer of solder have clearly demonstrated that a solder containing 45 per cent. tin and 55 per cent. lead is entirely efficient for general service, while the cost is materially less.

The composition specified for wiping solder is practically standard among all large users of this material.

As specifications of this nature should be adapted to the needs of the greatest number, an attempt has been made to insert such requirements as would guarantee a satisfactory product, but, at the same time, not needlessly limit the method of manufacture. Copper and zinc have been entirely prohibited as the former affects the flowing qualities while the latter produces brittleness. Antimony, however, up to a small percentage, is not detrimental and has not, therefore, been entirely prohibited. The other common impurities are not harmful if present in but small amounts. The requirements, therefore, allow the presence of metals other than lead or tin (excepting copper and zinc) up to 0.5 per cent. It is the opinion of the committee that this will allow the use of old metal of a suitable nature, but will prevent careless manufacture or wilful sophistication.

It was deemed wise to include in these specifications methods of analysis, as it is particularly essential in the event of controversy that all parties concerned should use the same analytical procedure.

Caustic Soda.—The sub-committee on specifications for caustic soda has submitted a report, but there are several important considerations in connection with this upon which your committee desires further time. The majority of the sub-committee, and many others consulted, agree that the so-called New York and Liverpool test for grading by the percentage of sodium oxide present is erroneous and that a change should be made to some system of grading according to the percentage of NaOH present. The manufacturers do not agree to this, but prefer to retain the present system. The sub-committee, also, does not agree to the necessity of incorporating in the specifications methods of sampling, but your committee feels that this is of the utmost importance.

Turpentine.—The sub-committee on turpentine has promised to submit its report at Indianapolis, and there will not be opportunity, therefore, for its consideration by this committee.

Incomplete reports have been submitted within the past few days by the sub-committees on soda ash, alum, nitric and mixed acids, muriatic acid and sul-

phuric acid specifications, which your committee has not had the opportunity to consider but which, in event of the continuance of this work, will be referred back to the sub-committees for further action.

The sub-committee on sulphuric acid specifications has been handicapped by the difficulty experienced in securing a third member.

Your committee has encountered considerable inertia on the part of the various sub-committees. The chairman of one of the committees reports:

"For ordinary purposes no one suffers from lack of specifications and any one using for special purposes enough to be benefitted by specifications would have the benefit of a chemist's services and procure without difficulty the article desired."

A member of another committee writes that he has "not been able to gather very much information on this subject as the specifications appear to be very simple."

Your committee also finds that owing to the geographical distribution of the members it has been difficult to make as much progress as we had hoped. In the case of nearly every sub-committee there has been a delinquent member who has delayed the work of his committee by not attending to correspondence. In one instance, a report prepared by a chairman was submitted to the other members of the sub-committee on January 6th and no reply had been received up to May 18th. These are merely examples to illustrate the difficulties encountered in committee work where members live a great distance apart. Any remedy for such conditions would greatly facilitate the progress of the work.

Respectfully submitted in behalf of the Committee,
H. J. SKINNER,
Chairman.

STANDARD SPECIFICATIONS (PROVISIONAL) FOR BLEACH.

Definition of Terms.—The word "Purchaser," where occurring in these specifications, shall mean the purchaser of the material hereinafter referred to or his duly authorized representative.

The word "Contractor," where occurring in these specifications, shall mean the party accepting the order to furnish the material hereinafter referred to, or his duly authorized representative.

General Description.—The material desired under these specifications is bleaching powder or calcium hypochlorite, prepared by absorbing chlorine in slaked lime. It must be white in color, fresh and dry.

Requirements.—The bleaching powder supplied under these specifications must test as follows:

1. It must contain not less than thirty-one (31) per cent. of available chlorine.
2. It must settle readily and completely when mixed with water. If lumps are present, they must break down and leave no core.

Basis of Price.—The base price per ton-unit named in the contract shall apply to bleaching powder containing thirty-five (35) per cent. of available chlorine and is represented in the table below as "1.00;" for variations from thirty-five (35) per cent. in the average of the whole shipment bonuses and penalties

shall be applied as per the table, provided the strength of no single package varies more than one (1) per cent. from the average of the whole and in no case falls below thirty-one (31) per cent., otherwise the entire shipment is to be at the disposal of the contractor or accepted under such terms as may be agreed upon.

Containing not less than:

31 per cent. base price $\times 0.74$ = price to be paid per ton-unit for whole lot.

32 per cent. base price $\times 0.82$ = price to be paid per ton-unit for whole lot.

33 per cent. base price $\times 0.89$ = price to be paid per ton-unit for whole lot.

34 per cent. base price $\times 0.95$ = price to be paid per ton-unit for whole lot.

35 per cent. base price $\times 1.00$ = price to be paid per ton-unit for whole lot.

36 per cent. base price $\times 1.04$ = price to be paid per ton-unit for whole lot.

37 per cent. base price $\times 1.07$ = price to be paid per ton-unit for whole lot.

38 per cent. base price $\times 1.09$ = price to be paid per ton-unit for whole lot.

39 per cent. base price $\times 1.10$ = price to be paid per ton-unit for whole lot.

Inspection.—All shipments shall be inspected and weighed upon arrival at destination. A sample shall be taken from every third or fifth package, according to the size of the shipment, the number of packages sampled, however, not being less than twenty (20) per cent. of the number in the shipment, and submitted to the tests described below. The sample shall be taken by boring a one- (1) inch hole through the side of the cask, midway from the ends, or through the head near the center. The sampler, which consists of a stout iron scoop about three-fourths ($3/4$) of an inch wide and eighteen (18) inches long, shall be inserted for two (2) or three (3) inches, withdrawn, and the bleach removed discarded. The sampler shall be inserted again as far as it will go, removed, the bleach transferred to a glass fruit jar, and the jar closed until the next cask is sampled. The hole in the cask shall be closed with a bung. The portions from the several casks shall all be mixed together to make one composite sample representing the shipment.

Analyses shall be made in accordance with the method given in Sutton's "Volumetric Analysis", 9th edition, page 175, Penot's Method, by adding an excess of $N/10$ sodium arsenite solution and titrating excess with $N/10$ iodine solution.

Method of Shipment.—All bleaching powder supplied under these specifications must be packed in strong, tight containers, entirely protected from air and moisture. Each package must be marked at the factory with the gross, tare and net weights and at serial number to identify it. Casks or drums which have been broken or the contents of which have been wet may be rejected at the discretion of the purchaser.

Failure to Meet Requirements.—Any shipment which fails to meet the requirements hereinabove specified

may be rejected and returned, the contractor paying freight charges both ways.

STANDARD SPECIFICATIONS (PROVISIONAL) FOR SOLDER.

Definition of Terms.—The word "Purchaser," where occurring in these specifications, shall mean the purchaser of the material hereinafter referred to, or his duly authorized representative.

The word "Contractor," where occurring in these specifications, shall mean the party accepting the order to furnish the material hereinafter referred to, or his duly authorized representative.

General Description.—The solder desired under these specifications is a homogeneous alloy of lead and tin, uniform in composition, containing no zinc or copper and as free from every other substance as possible.

Rosin flux solder shall consist of a shell of solder in the form of a wire, containing a core of rosin flux. Mineral and other non-resinous fluxes shall not be used.

The quality of the material used and the methods of manufacture shall be such as to insure for the completed solder the properties called for in these specifications.

Requirements.—1. The composition of the various solders supplied under these specifications shall be as follows:

Quality of solder.	Minimum per cent. of tin.	Per cent. of lead.	Maximum per cent. of metallic impurities other than copper and zinc.
Fine solder (bar solder) . . .	45	about 55	0.5
Wire solder	45	" 55	0.5
Rosin flux wire solder . . .	45	" 55	0.5
Wiping solder	40	" 60	0.5

2. The rosin core used in rosin flux wire solder shall be of commercially pure rosin and shall form not more than six (6) per cent. nor less than three (3) per cent. of the total weight of the finished product.

Inspection.—Each shipment shall be inspected and weighed. Drillings taken from any portion of each lot of solder shall be analyzed and the results of the analysis shall be considered to represent the composition of the lot.

Analyses shall be made in accordance with the standard method attached to and hereby made a part of these specifications.

Method of Shipment.—The completed solder shall be furnished in such form and weight and with such marks as may be specified.

Failure to Meet Requirements.—Any shipment which fails to meet the requirements hereinabove specified may be rejected and returned, the contractor paying freight charges both ways.

METHOD OF ANALYSIS SOLDER.

Preliminary Examination.—Make a qualitative analysis of the solder to determine what ingredients are present and to secure an indication of the amounts of impurities.

Note.—If any zinc or copper is found, further analysis of the solder is unnecessary. If these metals are

absent, proceed with the analysis in accordance with the following method:

Antimony.—Weigh $\frac{1}{2}$ gram of clean, bright drillings or clippings in a 450 cc. Erlenmeyer flask; add 10 to 15 cc. concentrated H_2SO_4 and heat until the alloy is thoroughly decomposed (this is generally accomplished in about 30 minutes from the time the fumes of SO_3 begin to come off). Cool the solution and add 300 cc. of water and 12 cc. of concentrated HCl ; boil in order to drive off all SO_3 , cool the solution and titrate rapidly with KMnO_4 (2 grams to the liter) which has been standardized against metallic antimony in exactly this same manner. The end point of the reaction takes place when a pink coloration is shown. After agitating the liquid, however, this pink will soon disappear.

Tin.—Weigh out 1 gram of clean, bright drillings or clippings into a tall 250 cc. beaker; cover beaker with watch glass and dissolve in 15 cc. of HNO_3 (sp. gr. 1.20); evaporate the solution to dryness on a hot plate, cool, add 40 cc. of HNO_3 (2 per cent.), and boil until residue is completely disintegrated. Filter and thoroughly wash with HNO_3 (2 per cent.). Place filter and contents in porcelain crucible, smoke off the paper, ignite for 15 minutes in full heat of Tirrell burner, cool in desiccator and weigh.

Note.—This precipitate contains the tin and antimony in the form of SnO_2 and Sb_2O_3 and also a small quantity of lead. To determine the amount of lead retained by the precipitate, proceed as follows:

Fuse the above precipitate with a mixture of finely powdered sulphur and soda ash in the proportion of 1 part of precipitate to 3 parts each of the sulphur and soda ash in a covered crucible until the odor of SO_2 has disappeared. Cool and dissolve the fusion in hot water. Add an excess of sodium sulphite to convert any polysulphides to monosulphides. Filter and wash thoroughly the precipitate of lead sulphide.

Note.—The tin goes into solution as sodium sulphostannate and the lead is quantitatively precipitated as lead sulphide.

Dissolve the precipitate of the lead sulphide in dilute nitric acid (1 part of HNO_3 to 4 parts of H_2O), add 5 cc. of strong H_2SO_4 (sp. gr. 1.84) and evaporate until the fumes of SO_3 are given off strongly. Cool and dilute with 200 cc. of water; boil, cool, add 100 cc. of alcohol and allow to stand in the cold for several hours; filter on weighed Gooch crucible, wash with 5 per cent. solution of H_2SO_4 and then with a mixture of 1 part of alcohol and 1 part of water until the washings are free from acid. Dry to constant weight at 105°C . and weigh as PbSO_4 .

$$\text{PbSO}_4 \times \log \text{factor } 9.86681 = \text{PbO.}$$

$$\text{PbSO}_4 \times \log \text{factor } 9.83449 = \text{Pb.}$$

From the weight of the precipitate of impure tin and antimony oxides subtract the weight of PbO and Sb_2O_3 previously determined. Calculate the remainder to metallic tin.

Factors.—

$$\text{Sb} \times \log \text{factor } 10.102511 = \text{Sb}_2\text{O}_3.$$

$$\text{SnO}_2 \times \log \text{factor } 9.89657 = \text{Sn.}$$

Lead.—To the original filtrate and washings from the precipitate of tin and antimony oxides, add 15 cc. of concentrated H_2SO_4 (sp. gr. 1.84) and evaporate the solution until the fumes of SO_3 come off strongly. Cool and dilute with 200 cc. of water; boil, cool, add 100 cc. of alcohol and allow to stand in the cold for several hours; filter on weighed Gooch crucible, wash with 5 per cent. solution of H_2SO_4 and then with a mixture of equal parts of alcohol and water until the washings are free from acid. Dry to constant weight at 105°C . and weigh as PbSO_4 .

Factor.—

$$\text{PbSO}_4 \times \log \text{factor } 9.83449 = \text{Pb.}$$

To the weight of lead so obtained add the amount of lead previously determined in the tin precipitate. This will give the total percentage of lead in the solder.

COMMITTEE ON STANDARD SPECIFICATIONS.

H. J. SKINNER, *Chairman*

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS— REPORT OF COMMITTEE ON CHEMICAL ENGINEERING EDUCATION.

Received July 3, 1911.

The Committee on Chemical Engineering Education was created at the Pittsburg meeting, December, 1908, and under the leadership of its able Chairman, now our worthy President, has done a great deal of valuable work since that time. It has conducted a great deal of correspondence, compared the existing courses of study for chemical engineering students in several of the best American and European schools, and made two lengthy reports, one in June, 1910, at the Niagara Falls meeting, and one in December, 1910, at the New York meeting. Both of these reports led to animated and instructive discussions, to the preparation and presentation in December last of the valuable papers of F. W. Atkinson and M. C. Whitaker, and to the sending out of a circular letter with a series of queries to be answered by the membership of the Institute. Unfortunately, the election of Dr. Frerichs to the presidency of the Institute made it necessary for him to relinquish the chairmanship of the committee, and in reconstructing the committee a chairman was selected who has not had the opportunity to make the recent exhaustive study of the subject that Dr. Frerichs has made, and must therefore apologize to the Institute for his inability to cover the ground in the thorough way in which the former chairman would certainly have done it. However, we fortunately have our President in our midst and can count upon his participation in the discussion and his counsel in arriving at a judicious conclusion to the same, and we have upon the committee several members who have already made valuable contributions to the study of the problem and who will further aid us in arriving at a solution worthy of the Institute.

To review briefly the work that has been done by the committee and to note the results thus far achieved, we find in the Bulletin of the Institute, issued in August, 1910, the text of a circular letter sent out by Dr. Frerichs, as chairman, under date of Feb. 4, 1910, which contained as a basis of discussion a synopsis of the course in Chemical Engineering of a typical

American university, and seven questions designed to elicit an expression of opinion as to what should be considered the proper course for a would-be chemical engineer. Of the replies received to the circular letter, four are embodied in the report made at the meeting of the Institute in June, 1910, *viz.*, those of Messrs. McKenna, Wiechmann, Veillon and Booth. These are given consideration in the report of the committee which follows and certain of the views and conclusions of the writers indorsed and farther elaborated. The verbal discussion at the Niagara Falls meeting was participated in by Messrs. Olsen, Baker and McKenna. Attention is particularly drawn to the valuable list of desirable subjects for post-graduate study in a chemical engineering course, given at length on pp. 30 and 31 of the Bulletin, to which reference will be made again. At the meeting held in New York in Dec., 1910, the subject of Chemical Engineering Education received a large amount of attention, the first session of the meeting being specially set apart for its consideration and discussion. The committee reported that additional communications on the subject had been received by them, mentioning those of Dr. Zwingenberger, Horace G. Byers, Wm. D. Richardson and Wm. M. Grosvenor, and the last-mentioned communication was read in full by the committee in connection with its report. However, without wishing to appear invidious, the most important feature of the first session was the presentation of the two carefully prepared papers of F. W. Atkinson and M. C. Whitaker, the one on "The Development of the Chemist as an Engineer" and the other on "The Training of Chemical Engineers."

Each of these papers, which are published in full in the Bulletin of December, 1910, was concluded by a series of questions designed to elicit an expression of opinion from members of the Institute. These questions, which cover pretty fully the ground gone over in the two papers, were then printed and made the subject-matter for Circular No. 2 of the Committee on Chemical Engineering Education, which has been sent by our Secretary to every member of the Institute as well as to a number of prominent educators in scientific schools and some men directly connected with important chemical industries.

With the answers that have come in reply to their circular letter and the previous expressions of opinion, to which reference has been made, we have all told the views of 37 men before us—not an overwhelming expression, it is true, but enough to furnish us with material upon which to build conclusions and perhaps arrive at some definite expression of opinion upon the main points at issue.

These replies have been tabulated so as to enable one to see how each of the 19 questions has been received and to allow us to arrive at some consensus of opinion upon most of them. Most of this tabulation was done in a very careful and painstaking way by the former chairman of the committee, Dr. Frerichs, and we have but transferred to his sheets the answers of a few whose replies came in late.

As it is obviously impossible for the Committee to present in extenso the replies and comments on the 19 questions, contained in even so moderate a list of letters, we will take up first the views on question 2, "Is the prevailing system of education adequate to produce the chemical and engineering talent needed in the industry?" Of 28 specific answers to this question, 8 gave a qualified approval to present methods, and 20 a more or less emphatic "no."

In addition to this showing, we have the letters published in the August and December Bulletins which reply to Dr. Frerichs' somewhat similar question, when, having given in full the four-year course of a typical American university, he asked "Is, in your opinion, a chemist having completed a four-year course as offered at this university and possessing the degree of B.S., satisfactorily equipped to enter practical work?" The five answers to this question in the published letters were all "no."

It may be assumed that under the "prevailing system of education" was meant in the minds of those who replied a four-year course of the typical kind given by Dr. Frerichs in his first report. This is, in fact, stated by several. Professor C. F. Mabery, of the Case School of Applied Science, Cleveland, says in his answer to this question, "needs a course of five years," and later he states what a fifth year should cover. It may be remarked incidentally that several of the technical schools have already made the course in Chemical Engineering a five-year course, as the Mass. Institute of Technology and the Brooklyn Polytechnic Institute, but relatively recently.

If we turn now to question 8, "Of what should the course in applied or technical chemistry consist? Specify the subjects to be taken and the proficiency to be acquired in each." If we could have a complete answer to this question, the entire problem would be solved. Unfortunately, we do not have such an answer. More than half of those replying to the circular declined to answer this question, and many of the answers given were quite indefinite and made no attempt to be complete.

Several of the replies, however, show such positive convictions as to what should or should not be taught that the Committee feels justified in quoting two of these expressions in full. The first is from a teacher, but one who has had exceptional opportunity to study manufacturing chemical processes by actual inspection in the works, and the other is from one of our younger members, who is the manager of a successful chemical plant and has had a wide range of experience.

"In most Chemical Engineering courses students spend entirely too much of their valuable time in college in playing with 'chemical practice.' The college is no place to teach a man the practice; it is a place to train him to think scientifically, and to handle the instruments of scientific investigation, making use of their results.

"Practice should be learned only in the works—by being employed or by systematic visits. A man can learn more of practice in four months in the works

than the university can teach him in four years, and learn it better. Accepting that, use the time in the university to teach him *what he cannot acquire outside*, to do anything else is to waste his time.

"JOS. W. RICHARDS,
"Bethlehem, Pa."

"No Chemical Engineer can be a specialist in all or even many branches of the industry.

"Schools should equip men to think independently, thinking to be based on a broad general scientific knowledge.

"Most graduates have poor preparation in physics, mechanics and engineering branches.

"The student who is going to make a truly meritorious and successful career in chemical engineering will get his broad training in fundamentals from the college theorists, and coincidentally his practical ideas from *independent* and absorbed pursuit of the applications by study of the current journals, visits to every available factory, talks with practical men of every line of industry he can connect up with.

"In my humble opinion, base no contact with both engineering and chemical industries and with college instructors, I regard it absolutely beyond reason to expect up-to-date, virile, practical instruction in the applications of theory to factory work, from those equipped to teach theory and in my experience it is the attempted '*practical*' teaching that the graduate must unlearn after he gets into practical work. No real success can follow without a broad grasp of physical laws of every kind taught in physics, and engineering, be obtained.

"If a chemical engineering graduate is to command and direct the work of chemists, laborers and mechanics, he must be able to see further than they can, have full confidence in his grasp of physical laws, and above all he must have it in him to make a leader, else no amount of learning will avail.

"THOMAS GRISWOLD, JR.,
"Midland, Mich."

Turning now to the equally important question, No. 19, of the Circular No. 2, we are asked, "What, in your opinion, is the main cause of the failure of the present courses in chemical engineering to produce men who are prepared in the best possible way for practical work in the manufacturing establishments of the United States?"

This question assumes that the present courses, considered broadly, are failures from the point of view stated. Several of those answering this question do not concede this to have been the case. As well presenting this view, the Committee will quote the language of an experienced educator, who is the head of a chemical engineering course in one of the most prominent technical schools of the country.

Henry P. Talbott, of the Massachusetts Institute of Technology, says: "I should not admit that all are failures. Some lack all engineering features and contain what some might call academic instruction in chemistry, mathematics, and mechanics, without any real correlation.

"It seems to me that those charged with the educa-

tion and training of the chemical engineer are confronted with an exceptionally difficult problem just now. It is a composite profession and in a very unformed state as yet. To an even larger extent than is the case with the older engineering professions, the scientific and technical progress has outrun the ability of the educational forces to keep pace with the increased demands, and I must confess that I feel that there is a rather unreasonable impatience in some quarters. An educational experiment which fundamentally affects the first year of a professional course requires about seven years for its completion, since three years after graduation is a minimum time in which to judge of results. Some of the best of our chemical engineering courses have not been in operation, in their modern form, as long as that.

"This is *not* equivalent to saying that they cannot or ought not to be improved, but I do not think that they have yet been fairly tested.

"To give fundamental instruction in fundamental chemical and engineering subjects demands the whole of four college years. This leaves little or no time for *applications*, and this apparently is our weak point. As compared with the civil, or electrical engineer, of mechanical engineer, the chemical engineer at graduation is at a disadvantage, for he has not had any practice at his profession, which is really the *combination* and *practical application* of the *two* branches of his training. The remedies seem to be (a) an extra year, which is costly, but may be necessary; (b) required summer work. In either case something must be provided on which he can practice. While I believe that the industries could help us a great deal, and benefit themselves by offering opportunities for summer employment, it is not now probable that they will do so to an extent which will remedy our all-edged defects. The other alternative seems to be the erection of laboratories which imitate, so far as may be, the conditions of a manufacturing plant, and I am inclined to favor development of such laboratories as far as resources permit, but there are serious questions still to be answered, both with respect to details and to available time, which will retard progress for a time yet. I am not clear as to the development of the *business* aspects (beyond a knowledge of accounting)."

Still more pointed in answer to question 19 are the remarks of one of our members, who has followed an earlier teaching career by years devoted to chemical manufacturing. The Committee will quote from the reply to the Circular No. 2, sent by Dr. Launcelot W. Andrews, of Davenport, Iowa.

"19. There appears to me to be two chief reasons for the shortcomings of the courses in 'Applied Chemistry.'

"One of these is general and is a fault of our entire educational system, the other is specific.

"The first lies in the fact that it is our educational practice to help the student far too much, to treat him as a recipient rather than an agent. His resourcefulness is not stimulated, his initiative not developed.

"The second consists therein, that his practical (that is laboratory) experience in chemistry is confined to reactions carried out on a very small scale and with apparatus to correspond. His thinking is in terms of test tubes and borax beads. If you speak to him of filtration, it means to him a three-inch disc of filter paper. He is unfamiliar with the tools he will have to work with, filter-presses, distillation-columns, large mills, tank reactions and with all the other aspects which chemical work has in the mind of the manufacturer. It is this ignorance of the tools of his trade that is the most serious obstacle he must overcome.

"The remedy is to be found in the equipment of laboratories with factory types of apparatus and in the institution of courses of study of such apparatus, determinations of their efficiency under various conditions, etc.

"In such study may easily be found a rich field for *research work*, which will tax the student's native resources to the limit, and will at the same time make him at home with his tools. Here is my partial answer to questions 8 and 9.

"There is much in these views in common with those advanced by Professor Whitaker, but with an important difference. Dr. Whitaker disclaims the intention to give the chemical engineering student instruction in special industries, while at the same time he advocates the erection of a model gas plant, or some other practical and complete plant, for instructional purpose. It is in the nature of the case that such a plant must be a mere imitation of the real thing, and I seriously doubt its value for the intended purpose. The same amount of time and money would probably bring in a much larger return if devoted to the separate study of those chemical manufacturing operations and appliances which constitute the elements or operative units out of which nearly every chemical factory is built up."

We think that the thought expressed in the last sentence of Dr. Andrews' remarks will bear study and developing.

Chemical manufacturing operations and appliances ought to be studied in both a descriptive and a practical way. Consider for a moment the variety of mixtures that have to be dealt with and from which values have to be extracted or created. The methods of extraction and separation in wet and dry ways, purification, and modification whereby the product acquires valuable properties can give rise to innumerable practical problems to be given to be worked out by the would-be chemical engineer. The economical handling of large quantities of materials, both end-products and lesser valuable side-products, should be studied in concrete examples as far as possible.

The former chairman of the committee, Dr. Frerichs, has given on pp. 30 and 31 of the Bulletin of Aug., 1910, a list of such lines of practical study that is very suggestive and shows some of the things that ought to go into a course for chemical engineers.

Then there are a few books, some in German and some in English, which take up for comparative

study the appliances and apparatus of manufacturing chemical works. We may mention Parnicke's "Maschinelle Hilfsmittel der Chemischen technik," Rauter's "Die Betriebsmittel der Chemischen Technik," and Oscar Nagel's "Mechanical Appliances of the Chemical and Metallurgical Industries."

The study in the class-room and in the technical school laboratories of working models of factory apparatus and the designing of modifications and special forms for varying conditions under an instructor who has had factory acquaintance ought to help materially in developing independence of thought on the part of an intelligent student.

Just as the making of preparations, both simple and more complex, is now considered a proper and necessary part of the work of the inorganic and the organic chemical laboratories, so the making of preparations on a small factory scale, using factory appliances and factory methods, and above all reckoning the cost of materials, time and labor, ought to be systematically practiced as a proper training for chemical engineering students. Our German brethren have published books covering this line of instruction also. I have a recent one which I found quite suggestive and of the type I have had in mind in referring to such exercises. It is called "Chemisches Prakticum, Präparative und fabrikatorische Uebungen," by A. Wolfrum, and is accompanied by an atlas on "Die apparate der chemischen technik und des laboratoriums, sowie die Einrichtung vollständiger betriebe," with many figures and tables.

However, the committee feel that it is not their province to go too much into detail concerning courses, but to present to the Institute what has resulted from the issuing of the Circular No. 2 to the Institute membership and would leave it to the Institute to determine what, if any, steps should be taken to give expression to our views in some formal or official way to those interested in chemical engineering education.

W. M. BOOTH,
A. A. L. VEILLON,
M. C. WHITAKER,
F. C. WIECHMANN,
SAMUEL P. SADTLER,
Chairman.

REPORT OF THE COMMITTEE ON QUANTITATIVE METHODS.

INDIANAPOLIS MEETING, A. C. S., JUNE, 1911.

Your Committee begs to submit the following report.

Since the time of the last meeting of this Section, it would seem that an unusual amount of work has fallen to the lot of the various members of the Committee, so it has been extremely difficult to make nearly the amount of progress which was anticipated. Some of the members of the Committee have found it impossible to do any work at this time, but this is off-set by the work of other members, who in the previous six months were likewise hindered from doing any work.

On February 2nd, the following assay process for mercury salts, as suggested by the chairman, was sent out.

Estimation as Mercuric Sulphide.—This method may be applied to all of the mercury salts used in the Pharmacopoeia by following the procedure indicated below.

Mercurous Chloride, Mercurous Bromide, Mercurous Iodide and Mercuric Iodide.—Weigh out accurately about 0.2 gram of the sample to be assayed, dissolve by the aid of 1 gram KI in 20 cc. water. Add 10 cc. 10 per cent. solution NaOH and then 3 cc. of 40 per cent. formaldehyde solution diluted to 10 cc. with water. Warm on a water bath for ten minutes or until complete precipitation of metallic mercury takes place. Decant through a Gooch filter and wash the precipitated mercury thoroughly with water. Dissolve off the filter with 2 cc. concentrated nitric acid, washing the filter carefully with water.

“(From this point on the process may be applied also to mercuric oxide, metallic mercury, ammoniated mercury, mercury with chalk and mercuric nitrate by solution in 2 cc. nitric acid and carrying out the following procedure.)

“Evaporate the solution to dryness on water bath and take up with 2 cc. concentrated hydrochloric acid and water sufficient to make 50 cc. of solution.

“(From this point the process is applicable to mercuric chloride by solution as above.)

“Precipitate the mercury from this solution in the cold by slow stream of hydrogen sulphide, let settle and filter through Gooch filter. Wash thoroughly with water and then three times with alcohol. In order to remove any sulphur precipitated along with the mercuric sulphide, the precipitate should now be washed with carbon disulphide, which may be accomplished most easily by the method given in *Treadwell-Hall*, Volume 2, page 89. After extraction for one hour wash once with alcohol and once with ether to remove the carbon disulphide. Dry at 100°–110° and weigh.”

It was requested that this be tried both with and without washing the precipitated mercuric sulphide with carbon disulphide.

Reports were received as follows:

Brown: HgCl with CS₂, 98.79 per cent., 98.82, 98.49, 99.44; average, 98.98 per cent.

HgI₂, with CS₂, 97.94 per cent., 97.28, 98.84, 98.91; average, 98.24 per cent.

Sy: HgCl, without CS₂, 98.84 per cent, 96.91, 98.41; average, 98.06 per cent.

With CS₂, 98.55 per cent., 96.91, 98.09; average, 97.86 per cent.

HgI₂, without CS₂, 93.24 per cent., 101.60, 82.64; average,

With CS₂, 93.24 per cent., 101.02,; average,

Taylor:

Comments of various members of the committee are as follows:

Mr. Brown: “I have tried out the sulphide method on the mercury samples as per your request,

but am not very well pleased with the method or the results.

“The method is tedious and long and there are too many chances for error to creep in. I find it very difficult to dissolve the reduced mercury off the asbestos pad completely. The proportion of mercury in the sulphide is very large, making any loss of mercury show up to a great extent when calculated to per cent. on the original sample.”

Mr. Murray: “I have always looked upon the method as a laborious one and have thought that the Committee of Revision also regarded it in that light.”

Mr. Sy: “I am unable to explain the results on the mercuric iodide. Washing with carbon disulphide seems to be unnecessary.”

Mr. Taylor: “One frequent objection to this method is the liability of precipitation of sulphur and the difficulty of washing with carbon disulphide. However, unless the solution is very strongly acid, the precipitation of sulphur is negligible. As an illustration of this, hydrogen sulphide was passed into 1 and 2 per cent. nitric acid and the strongly smelling solution was allowed to stand, but no precipitate or opalescence appeared within two hours. While the percentage of mercury in the sulphide is large, yet the loss with careful manipulation should be but very small. Experience with this method will, I believe, show that it is easy and rapid and fully as desirable as any of the volumetric methods which were presented at the last meeting.

“The solution of mercury compounds may also be accomplished easily by hydrochloric acid and potassium chlorate instead of nitric acid.

“This gives practically a solution of mercuric chloride and it only requires to blow cold air through the solution for about one hour to remove every trace of chlorine, this being the most important part of the process. See that no trace of chlorine remains in the solution.”

ZINC ASSAYS.

The following zinc salts of the Pharmacopoeia have the purity requirements as given but without any corresponding assay process:

Zinc acetate, 99.5 per cent.; zinc bromide, 97.0 per cent.; zinc carbonate, 72.0 per cent., ZnO; zinc chloride, 99.5 per cent.; zinc iodide, 98.0 per cent.; zinc phenolsulphonate, 99.5 per cent.; zinc stearate, 13.5 per cent., residue chiefly ZnO; zinc sulphate, 99.0 per cent.; zinc valerate, 99.0 per cent.; zinc oxide, 99.0 per cent.

Requests for suggestions on assay processes for these compounds were sent out on February 2nd and the following process was suggested by several members of the committee. This is the well known zinc ammonium phosphate method.

A cold solution of the zinc salt (0.5 to 1.5 grams) is very carefully neutralized or made slightly alkaline by the addition of ammonia with methyl orange and is made up to about 125 cc. Dissolve in this solution 5 grams of ammonium chloride and then add, with stirring, 50 cc. of 10 per cent. solution of diammonium hydrogen phosphate. Let stand on top of

water bath at nearly boiling temperature, for about one hour, or until the flocculent precipitate has become crystalline and the liquid clear. Cool and filter through a Gooch crucible, washing first with about 100 cc. of 1 per cent. solution diammonium hydrogen phosphate, then with about 500 cc. of water, followed by a little alcohol, and lastly ether. Make the washing a continuous operation, not letting the liquid get entirely off the precipitate until the end. Dry at 100° – 120° and weigh as NH_4ZnPO_4 . If desired, this may be ignited in the usual way and weighed as $\text{Zn}_2\text{P}_2\text{O}_7$.

Mr. Murray writes that "this method has been tried on zinc sulphocarbolate, valerate, acetate, stearate, oxide, etc., with promising results. The acetate and sulphocarbolate require no special treatment. The valerate dissolves upon addition of the ammonia. The stearate is freed from fatty acids by hydrochloric acid, filtration and washing before the zinc can be precipitated. The oxide must, of course, be dissolved in hydrochloric acid. Judging from present experiences, the method may be expected to give no trouble with the bromide, chloride, iodide, carbonate and sulphate of zinc, nor with the zinc metallic."

This process, while it has not been put to actual trial at this time on a special sample by the Committee, yet is perhaps the most reliable and efficient method we can find for the estimation of zinc and can be readily applied to all of the various compounds in the U. S. P. with some little variation.

Following the zinc salts, the Committee expects to take up such substances as are official in the Pharmacopoeia having the definite purity requirements without an assay process and go over them in alphabetical order. The Committee is desirous at this time of receiving any further suggestions or instructions from the section as a whole and will be pleased at any time to have their attention directed to work such as will be of interest or aid to them.

Committee on Quantitative Methods,
FRANK O. TAYLOR,
Chairman.

REPORT UPON THE THIRD NATIONAL CONSERVATION CONGRESS.

Sept. 25th, 26th and 27th, 1911.

The first session of the Congress opened at ten o'clock Monday morning, Sept. 25th, at Convention Hall, Kansas City. After a prayer by the Roman Catholic Bishop of Kansas City, addresses of welcome were given by Mayor Brown, of the City, Mr. J. C. Lester, of the Kansas City Commercial Club, and Gov. Hadley, of Missouri. Responses were made by Dr. Henry Wallace, President of the Congress, and Hon. J. B. White, Chairman of the Executive Committee. Dr. Wallace pointed out how the new conditions which gradually arose in this country caused a flow of population from the rural to the urban districts. He suggested remedies for this, namely, the improvement of agricultural conditions, and this was the subject

that was to receive especial consideration in this Congress. After announcements the session closed.

The second session was called to order at 2 P.M. After an invocation the chair appointed committees on resolutions, on nominations, etc. He then called for reports from state conservation commissions and other organizations concerned in conservation. The chief address of the afternoon was given by Hon. Benjamin Lindsay, Judge of the Juvenile Court of Denver, on the *Country Child* versus the *City Child*. The Judge held there was no essential difference between the two but that surroundings, manner of life, etc., of the country boy were conducive to a better development physically and morally than in the case of the city boy. He was not as sanguine as Dr. Wallace that the trend of population from the country to the city can be checked.

The third session was called to order at 8 o'clock. After preliminary addresses by state representatives, Present Taft gave the address of the evening on "*The Conservation of the Fertility of the Soil*." The President is optimistic and believes that although our methods of agriculture will have to be improved, owing to the fact that our population is growing at a greater rate than the increase in tillable land, we will still be able to feed our own population for many years from our own soil. The Department of Agriculture is doing much and plans to do more, to educate the farmer. With improved methods of farming the profits of the farmer will be more certain. The national and state Departments of Agriculture are working together for the purpose of placing in each country of every state an agricultural expert whose duty it will be to give instruction to the farmers of the county.

The fourth session opened at 10 o'clock, Tuesday, Sept. 26th. After prayer and routine business, reports from state and national organizations were continued. Papers were then read by Prof. P. C. Holden, on *Social Life on the Farm*, by W. A. Beard on *Cooperation*; and by H. Quick on *The Farmer and the Railroad*. Mr. Barrett, who was scheduled to speak on *The Farmers Educational and Cooperative Union of America* was prevented from being present by sickness.

The fifth session opened at 2 P.M. After prayer, announcements, routine business and reports of committees, addresses were given by Dr. Frederick B. Mumford, Dean of the University of Missouri, on *The Live Stock Farm and Soil Fertility*; by Mrs. Harriet W. Ashby on *The Farmer's Wife*.

The sixth session was called to order at 8 P.M. A paper was read by Mrs. Philip N. Moore on *The Community Club*. Dr. Warren H. Wilson made a forceful address on *The Church in the Open Country*. Then, after a most enthusiastic reception, Dr. Harvey W. Wiley spoke on *The Health of the People*. Dr. Wiley advocated the establishment of a national department of health in Washington, the secretary of which should be a cabinet member.

The seventh and eighth sessions were held on Wednesday the 27th inst. The printed program was

not rigidly adhered to; some of the papers scheduled for the afternoon were given in the morning. Hon. Curtis Hill spoke on *How Good Roads Help the Farmer*, Hon. J. B. White on *Practical Forestry in Europe and America*. A representative of the U. S. Department of Agriculture, W. J. Spillman, spoke in place of Dr. Bradford Knapp, who was absent.

He was followed by Prof. Cyril Hopkins, of the University of Illinois, on *Worn-out Soils*. This was a comprehensive and forceful address. He considered the chemistry of soil, emphasizing the necessity of using artificial fertilizers, especially ground rock phosphate, limestone and in some cases nitrogenous matter and potash, to restore worn-out soils. He made a remarkable statement, namely, that most soils contain an abundance of potash and do not require any further addition of this element. He also advocated the use of the raw untreated phosphate rock.

Dr. Hopkins urged that the large sums of money used to reclaim the arid lands of the west could be used to much greater advantage in restoring the fertility of the farms of the country that are located near the centers of population and that receive abundant rainfall. Dr. W. J. McGee read a paper on *The Trend of the Conservation Movement*. In the afternoon session the principal address was by the Hon. Walter L. Fisher, Secretary of the Interior, on the *Conservation of the Public Domain*. Mr. Fisher advocated the system of renting or leasing the coal lands and water power for a limited number of years and not letting the permanent possession go out of the hands of the people. Addresses were also made by Hon. W. B. Hoard on *Dairying and Soil Fertility*; by Prof. A. N. Ten Eyck, Kansas State Agricultural College, on *Proper Methods of Soil Cultivation*; by Mr. A. P. Grout on *The Rape of the Soil*.

The chairman of the Committee on Resolutions then read a long series of recommendations which were adopted unanimously by the Congress. Letters were read from Theodore Roosevelt, and the delegates sent a telegram of greeting to Gifford Pinchot.

At the evening and final session Mr. William Jennings Bryan delivered an address on *Phases of Conservation*.

EDWARD H. KEISER,
Delegate, A. C. S.

MEETINGS OF THE CHEMICAL SOCIETIES IN NEW YORK.

At a special meeting of the Chairman and Secretaries of the New York Section of the American Chemical Society, the American Electrochemical Society, and the Society of Chemical Industry, held at the Chemists' Club on October 3rd, a tentative program was outlined for meetings for the season 1911-1912. Three joint meetings have been arranged which promise to be of very wide interest.

PROGRAM.

October 6th.—American Chemical Society. New York Section.

October 20th.—Society of Chemical Industry. New York Section.

November 10th.—Joint meeting under the auspices of American Chemical Society. Subject: Symposium on Fuel Economy.

December 8th.—Regular meeting, American Chemical Society. Award of Nichols Medal. Election of Local Councilors.

December 13th.—Annual meeting; the Chemists' Club.

1912. January 5th.—Regular meeting; American Chemical Society.

January 19th.—Regular meeting; Society of Chemical Industry. Award of Perkin Medal.

February 9th.—Joint meeting; under the auspices of the American Electrochemical Society. Subject: Research.

March 8th.—Regular meeting; American Chemical Society. Election of Officers of the Section.

March 22nd.—Regular meeting; Society of Chemical Industry.

March 29th.—Regular meeting; American Electrochemical Society.

April 19th.—Joint meeting; under the auspices of the Society of Chemical Industry. Subject: Alkali.

May 10th.—Regular meeting; American Chemical Society.

May 24th.—Last regular meeting; Society of Chemical Industry.

June 7th.—Last regular meeting; American Chemical Society.

PROGRAM OF FIRST JOINT MEETING OF NEW YORK CHEMICAL SOCIETIES.

The first joint meeting of the New York Sections of the American Chemical Society, American Electrochemical Society and Society of Chemical Industry, is scheduled for November 10th, at the Chemists' Club, and the program will be a general symposium on Fuel Economy.

PROGRAM.

"Fuel Gasification for Industrial Purposes." By Professor Charles E. Lucke.

"A Continuous Carbon Dioxide and Temperature Recorder and Its Application to Combustion Efficiency." By Edward A. Uehling.

"Is Peat an Important Fuel?" By Charles F. McKenna.

"Deterioration and the Fire Risk in the Storage of Coal." By H. C. Porter.

"The Distribution of Heat in Boiler Plant Operation." By Perry Barker.

"Some Attempts at Economy in Making Steam." By J. W. Loveland.

NATIONAL ACADEMY OF SCIENCE.

By invitation of the trustees of the New York Public Library the autumn meeting of the National Academy of Sciences will be held in its new building, Forty-second Street and Fifth Avenue, beginning on Tuesday, November 21st. The first business meeting of the Academy will be held on Tuesday morning at eleven o'clock and the first open scientific session will be at two o'clock in the afternoon.

OHIO SOCIETY OF MECHANICAL, ELECTRICAL AND STEAM ENGINEERS.

November 17-18th. Annual meeting at Canton, Ohio. Secretary, F. E. Sanborn, Ohio State University, Columbus, Ohio.

NEW JERSEY SANITARY ASSOCIATION.

November 24-25th. Annual meeting at Lakewood, N. J. Secretary, J. A. Exton, 75 Beech St., Arlington, N. J.

AMERICAN PUBLIC HEALTH ASSOCIATION.

December 4-9th. Annual meeting at Havana, Cuba. Secretary, Wm. C. Woodward, Washington, D. C.

ASSOCIATION OF AMERICAN PORTLAND CEMENT MANUFACTURERS.

December 11-13th. Annual meeting at New York City. Secretary, Percy H. Wilson, Land Title Building, Philadelphia, Pa.

AMERICAN SOCIETY OF MECHANICAL ENGINEERS.

December 5-8.—Annual convention at New York City. Secretary, Calvin W. Rice, 29 West 39th St., New York City.

NATIONAL SOCIETY FOR THE PROMOTION OF INDUSTRIAL EDUCATION.

November 2-4.—Annual meeting at Cincinnati, Ohio. Secretary, Edward H. Reisner, 20 West 44th St., New York City.

Professor Alexander Smith, President of the American Chemical Society, has made the following appointments:

Committee on Professional Ethics: A. C. Langmuir, Charles F. McKenna and Lucius P. Brown.

Committee on the Perkin Medal Award, 1912: W. R. Whitney, Chairman, W. R. Walker, W. D. Richardson, A. D. Little, F. B. Carpenter, W. H. Brady.

Delegates to the Meeting of the International Association of Chemical Societies: Theodore W. Richards, W. A. Noyes, A. L. Day.

The National Civic Federation has formed a new Pure Food and Drug Department. The first meeting was held in New York City on October 2nd. Among the speakers were Dr. Harvey W. Wiley, Chief of the Bureau of Chemistry, and Dr. Wm. C. Woodward, Secretary of the American Public Health Association.

The British Association for the Advancement of Science has recently made an appropriation for the furtherance of chemical study, classifying as follows: Gaseous Explosives, 300 dollars; International Commission of Physical and Chemical Constants, Dynamic Isomerism, and Plant Enzymes, 150 dollars each; the study of Hydro-aromatic substances, 100 dollars, and 50 dollars each to Electroanalysis and Transformation of Aromatic Nitro-amines.

Professor Charles L. Parsons was the representative of the American Chemical Society at the recent meeting in Chicago of the American Mining Congress.

The Society for the Promotion of Agricultural Science will hold its thirty-second annual meeting in Columbus, Ohio, on November 14th.

The Association of American Agricultural Colleges and Experiment Stations will hold its annual convention in Columbus, Ohio, beginning November 15th.

OBITUARIES

WILLIAM HENRY McLAUCHLAN.

Among the twelve spectators who lost their lives in the terrible accident at the New York State Fair Automobile Races, September 16, 1911, was Dr. William Henry McLauchlan, 41 years of age, Secretary of the Syracuse Section of the American Chemical Society, Editor of "The Syracuse Chemist" and a member of the Chemical Department of The Solvay Process Company.

Possessed of the highest scholastic attainments, Ph.B. University of Michigan 1893, M.S. Princeton 1899, and Ph.D. Breslau 1903, he was highly successful as an industrial chemist, in steel work, and in the manufacture of synthetic organic acids, and, lastly, with the Solvay Process Company, where he was in charge of important experiments on a manu-

facturing scale. Last winter he organized and carried on a course in Chemistry for some of the younger employees of the company, commenting in his droll way: "There's no reason why we shouldn't share some of the pie that we've had so much of."

Dr. McLauchlan was also an enthusiast in a wide field of activities: athletics, religious education, music, Boy Scouts, literary club and amateur theatricals form a list sufficiently long to indicate the breadth of his avocational interest. His cordiality and enthusiastic cheerfulness made him invaluable as an informal speaker and entertainer. No man could have been held in higher esteem by his associates and subordinates in the works and by outside acquaintances. Their strong sympathy goes to the bereaved wife and little daughter, Matilda Gill.

L. C. JONES.

NOTES AND CORRESPONDENCE.

To the Editor of the Journal of Industrial and Engineering Chemistry.

Reading an article in *Chemical Abstracts* on the "Detection of Graphite in Lubricants" (page 2550) it has occurred to me that the following might be of interest:

The residue of amorphous carbon and graphite should, according to Mr. J. Marcusson and Mr. G. Meyerheim, be separated by fusing with NaOH in a nickel crucible for fifteen minutes over a Bunsen burner and a few minutes' blast.

According to my experience it is right for certain very fine grades of lampblack and fine amorphous carbon from tar and pitch, but not so for coarse amorphous carbon from tar, pitch, coal, anthracite, charcoal, retort graphite, etc., and even a coarse grade of lampblack will fail to disappear under above conditions.

Besides a considerable loss is suffered when the graphite is fine, and the fineness in this instance not only means a certain sieve number but also thickness of flake, thus some graphite may be on a sieve No. 30 and measure 0.00045 and another grade on same sieve will measure 0.002 or more.

The loss thus suffered may be as high as 15 per cent. of entire carbon.

This must not be understood to mean that fineness is all, and that there is no difference—everything else equal, in resistance against chemical actions of the different grade of carbons.

A chemical examination alone of graphite to be tested gives very unsatisfactory results; thus the test for crystalline graphite to see whether it puffs up is unreliable entirely depending on fineness. If a certain graphite as Dixon's Ticonderoga or Ceylon respond to the test, same graphite when ground fine with sand and purified by washing, by HF, H₂SO₄, or KOH, etc., will not puff up.

The test with pure nitric acid and KClO₃ is troublesome and gives very little information when anthracite or retort graphite, etc., is in the mixture, and the amount of graphitic acid thus made depends on many outside circumstances beside the material being tested. Humidity in the air, size of vessel used, temperature, time, all are factors to be taken into account. Little reliance can therefore be placed on those tests, and physical test seems to me to be the most reliable. Graphitic carbon has a sp. gr. of above 2.2 and amorphous carbon has a sp. gr. of below 2. Ethylene bromide (Merck), C₂H₄Br₂, has a sp. gr. of 2.15 and as it can be used over again a number of times the expense is only trifling.

The method found most satisfactory is to take 1 cc. material to be tested in a graduated glass tube, shake it up with ethylene bromide and spin it around in a centrifugal machine. A clean separation is made, graphitic carbon on bottom and amorphous on top.

If sample is very impure a purification by HF + H₂SO₄ will help matters but, amorphous carbon

generally being pure, it is as a rule not necessary. A further separation of different amorphous carbon may be had by using other liquid mediums.

LABORATORY
JOSEPH DIXON CRUCIBLE CO.
JERSEY CITY, August, 1911

J. E. THOMSEN.

To the Editor of the Journal of Industrial and Engineering Chemistry.

Our attention has been called to an article in your July issue headed "Acetylcellulose Films withdrawn from the Market." The impression left in the reader's mind by the article is that the making of films on acetate base was abandoned by this company because its product failed to meet the requirements of the trade. Permit us to correct this impression. While it is a fact that those of our customers who had been using cellulose acetate film exclusively for nearly two years have returned to the use of the cellulose nitrate stock, we have not "abandoned the manufacture of these films," for we are still filling occasional orders for the acetate film and are prepared to manufacture on a large scale should a majority of our customers decide to return to the use of this film exclusively. The reason that the manufacture was discontinued was not because "the acetyl films were inferior in lasting qualities and the general trade objected to their use." It is true that the acetylcellulose film which was manufactured for several months after this product was introduced was inferior in wearing quality to the nitrocellulose film. But improvements in the process were made which resulted in a product that was in practical use substantially as durable as the nitrate film. At the time our customers gave up its use, and for a year previous, we were not getting complaints of a lack of wearing quality. So far as the product was concerned, we feel sure that our trade would have continued its use indefinitely. Having brought the acetate base to this point, we do not feel that there would have been any technically retrograde step if we had stopped its manufacture altogether. The regret is that cellulose acetate, even when manufactured in very large quantities, can not be made at a cost which would make it possible to sell the film at the same price as the nitrocellulose film. An advance of nearly 15 per cent. did not more than cover the extra cost of manufacture. The film went out of general use because the trade found that it had not displaced the nitrate film. The two were used together at the theatres. The safeguards with which municipalities and insurance companies surrounded the use of the inflammable film were still required, and the fact that no serious accidents occurred during the two years that the two films were used together in the theatres, shows that the protective devices and regulations were adequate. Therefore, that section of the film manufacturers using non-inflammable film could see no reason why

it should continue to bear the burden of a raw material of a higher cost than that used by its competitors, and returned to the use of nitrocellulose.

Trusting that the above somewhat lengthy statement will make the situation plain to your readers, we remain,

Yours very truly,

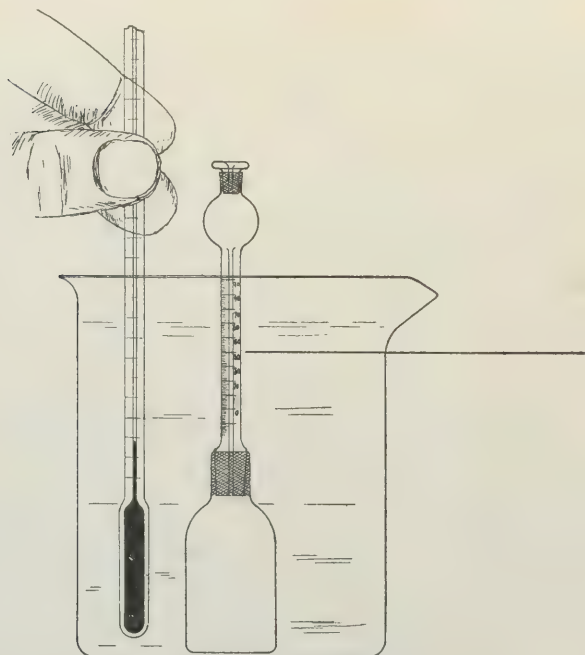
EASTMAN KODAK COMPANY.

ROCHESTER, N. Y.,
September 26, 1911.

NOTE ON THE DETERMINATION OF THE SPECIFIC GRAVITY OF ETHYL ETHER, U. S. P.

The following method for the determination of the specific gravity of ethyl ether has given satisfactory, practical laboratory results, varying not more than two points in the fourth decimal place.

A calibrated pycnometer of 25 cc. capacity, as shown in the sketch, is employed. To determine its volume the pycnometer is first weighed with water at 25° C., choosing a convenient mark on the stem, say 30 or 40, whichever may be more convenient, as indicated in the sketch by a line. The pycnometer is then filled with ether to a little above the mark



at which the weight of water has been determined and placed in a 1000 cc. beaker containing water which is carefully kept at 25° C. and constantly stirred with a thermometer. When the volume of ether becomes constant in the pycnometer the excess of ether is drawn off by means of a capillary pipette until the desired mark is exactly reached. The pycnometer is then quickly dried with soft flannel or filter paper and weighed. A capillary pipette for this purpose is easily made by drawing out an ordinary eye-dropper.

GEO. D. ROSENGARTEN.

LABORATORY OF THE POWERS-WEIGHTMAN-
ROSENGARTEN Co., September, 1911.

A METHOD FOR FILTRATION.

Analysts, and particularly those who are engaged in organic work, are frequently confronted with solutions containing precipitates which require a long time to filter and some indeed quite impossible.

The following will serve to illustrate: Subacetate precipitate in vanilla extract, jams, various crude drugs, wines, etc., gelatinous starchy solutions, macerated tissues in toxicological work, ferric and aluminum hydrates, and in fact any precipitate likely to clog the pores of filter paper, pulp or asbestos.

The writer, after having tried many schemes without success, has at last obtained most satisfactory results by means of an apparatus consisting of a suction pump, and a heavy side-necked Erlenmeyer flask, in the stopper of which is inserted a Büchner filter of convenient size. Over the holes is placed a double filter paper; this is wetted to fit tightly over the holes and the paper is then sprinkled evenly with coarse, acid-washed and ignited sea sand to a depth of from 1-1½ cm.

The filtration may then be begun.

The same idea may be used for the preparation of Gooch crucibles in weighing precipitates dried in the air bath.

HALSEY DURAND.

DEPARTMENT OF HEALTH,
NEW YORK CITY.

GENERAL NOTES.

Professor W. E. Adeney, F. I. C., curator and ex-Examiner in Chemistry of the Royal University of Dublin, arrived in New York City on October 7th, to consult with the Metropolitan Sewerage Commission of New York on questions relating to the assimilation of sewage by harbor waters. Dr. Adeney is distinguished for experimental researches in chemistry, the results of which have been published largely in the Transactions of the Royal Dublin Society and in the Proceedings of the Royal Irish Academy. With Professor Letts, of Belfast, he contributed a notable monograph on the pollution of estuaries and tidal waters with a description of experimental researches into the phenomena of the digestion of sewage by water, which was published as Appendix VI. of the Fifth Report of the Royal Commission on Sewage Disposal.

A sulfuric acid plant with an annual capacity of 25,000 tons of acid is being erected in Corey, Ala., by R. A. Brown & Company.

A committee dealing with the hygienic aspects of illumination has been appointed by the Minister of the Interior in France. The objects of the committee include the general effects of illumination on health, the framing of simple rules as to the best means of applying customary systems of lighting to various industrial operations, the nature and causes of short sight and impairment of vision, and their connection with defective living conditions, the study of methods of measuring illumination, etc.

Wm. P. Buchanan, a prominent chemist of Philadelphia, died on September 23rd as the result of burns sustained during an explosion of flash-light powder with which he was experimenting.

Dr. Davenport Fisher, formerly professor of chemistry at the Annapolis Naval Academy, lately consulting chemist in Milwaukee, was killed by a street car on October 11th at the age of 80 years.

The Eastern Blau Gas Co. has commenced erecting its new works at Portland, Me.

Dr. Harvey W. Wiley, Chief of the Bureau of Chemistry, U. S. Dept. of Agriculture, has received the honorary degree of Doctor of Laws from the University of Vermont, on October 6th.

Dr. Edward Renouf, Collegiate Professor of Chemistry at Johns Hopkins University since 1890, has retired from active service.

Dr. Leon I. Shaw has been appointed instructor in chemistry at Northwestern University.

W. A. Whitaker, Jr., of the chemistry department of the College of the City of New York, has been appointed associate professor of metallurgy at the University of Kansas.

Dr. J. P. Montgomery, of the Mississippi Agricultural and Mining College, has been appointed adjunct

professor of chemistry at the Alabama State University.

Mr. Earle O. Whittier has been appointed instructor in chemistry at the University of Maine.

Dr. Alex. Findlay, special lecturer at the University of Birmingham, has been appointed professor of chemistry at the University of Wales.

Mr. Herbert T. Salmonde has been appointed chemist and bacteriologist at the Memdale filters, in Springfield, Ill. He is leaving the Chicago Board of Health to take up his new work.

The Second Annual Cement show will take place in New York City in Madison Square Garden, Jan. 29th to Feb. 3rd, 1912.

The acid chamber building of the Etiwan Fertilizer Co., of Charleston, S. C., was totally destroyed by fire recently, entailing a loss of \$50,000. It will be rebuilt immediately.

A fifty-acre piece of level land recently reclaimed on the Cambridge side of the Charles River basin, between the Harvard and West Boston Bridges, has been selected for the new site of the Massachusetts Institute of Technology. The selection is contingent on favorable action by the city of Cambridge in closing up certain streets.

CONSULAR AND TRADE NOTES.

PROPOSED TEXTILE BUREAU IN GERMANY.

The Correspondenz der Aeltesten der Kaufmannschaft (Berlin) of July 31st contains the copy of a resolution introduced in the Reichstag last March on the subject of the establishment of an Imperial Textile Bureau. It was proposed that the bureau should be used not only as a conditioning house, but also as a central office for the encouragement of the German textile industry generally. It was intended to encourage the use of genuine instead of imitation material as regards dyes, to aim at the universal adoption of the metric system in the counting of yarns, to combat the weighing of silks, and to carry out investigations as to technical improvements. The Aeltesten der Kaufmannschaft has now forwarded a note to the Ministry of the Interior deprecating the establishing of the bureau in question, owing to the impracticability of making one central office responsible for so many and such widely varying objects.

AMERICAN TRADE IN CEMENT.

Cement imports into the United States have fallen away rapidly in the last few years. The value of Roman, Portland, and other hydraulic cements imported in 1907 was \$3,669,926; in 1908, \$1,973,472; in 1909, \$712,628; and in 1910, \$602,833. Of the total for 1910, Germany furnishes \$291,635 worth and Belgium, \$160,374. Exports of cement from the United States have increased in value from \$1,180,415 in 1907 to \$2,292,376 in 1910. Of the latter amount, however, \$1,228,893 worth went to Panama. The two consumers next in importance were Cuba with \$458,063 worth and Mexico with \$161,696.

BRITISH LABOR STATISTICS.

Since 1906 the British Board of Trade has been conducting an inquiry in reference to the earnings and hours of labor of workers in various industries, including agriculture, in the United Kingdom. The result of the inquiry so far as it concerns the metal, engineering and shipbuilding trades has recently been published.

The table that follows gives the number of employees in each of the seven principal trades dealt with in the report, together with their average weekly earnings, the total wages bill for the year, the average number of hours worked per week, and the holidays per year:

Industry.	Number of employees.	Weekly earnings.	Total wages for year.	Hours per week.	Holidays per year.
Engineering, etc.	368,552	\$6.29	\$126,576,828	53.1	13.4
Iron and steel.	53,981	8.75	20,589,397	54.4	12.4
Light iron castings, etc.	12,333	5.97	3,395,926	53.8	11.5
Pig iron.	13,995	8.10	5,321,827	53.2	7.3
Railway-carriage building.	45,829	6.62	14,549,117	53.6	7.3
Shipbuilding, etc.	109,285	7.43	40,362,074	52.9	10.8
Tin plate.	10,921	7.79	3,712,137	47.8	10.8

In the other metal trades investigated the average earning of men working a full week were highest in the manufacture of jewelry, the amount being \$9.23, and the lowest in farriery and general smith's work, where the average was \$6.74. It is estimated that the annual average earnings for those engaged in the manufacture of chains, anchors, etc., were \$404, while \$204 represented the annual earnings of those engaged in the manufacture of needles, fishhooks, and fishing tackle.

NEW ARTIFICIAL SILK MILLS IN RUSSIA.

Independent of the factory for making artificial silk in course of construction at Tomashovo, Poland, a new \$772,000 association (*Société Anonyme des Soieries de Sakhatshev*) is being founded for erecting mills to make artificial silk on the Chardonot system. The factories will be built at Barishev, near Sakhatsche Station of the Kalish Railway in Poland. The head office will be in Brussels and the general agency in Warsaw. Large quantities of artificial silk yarn have been steadily imported into Poland, but as the import duty thereon is only slightly less than on the genuine, its utilization for weaving into fabrics has been rather hampered.

PURE AIR IN LONDON TUBES.

Deputy Consul General Carl R. Loop.

One of the strongest objections made to traveling underground in London is the fact that the air is impure and often stifling. What promises to be a revolution in this particular is a plan which has recently been announced by the authorities

of the Central London Railway Co., according to which a system of ventilation will be installed capable of pumping daily 80,000,000 cubic feet of ozonized air into the tube stations and tunnels of that company.

One plant is already in operation and it is hoped that similar ones will soon be completed at every station along the line. It is stated by one of the officials that the plant at each station will pump 400,000 cubic feet of air per hour into the station, or at the rate of 900 cubic feet per person per hour. The ordinary allowance in buildings is about 300 cubic feet of fresh air per person.

The air is drawn from outside through a filter screen, which removes dust and dirt and impure gases. A part of the air is then highly ozonized by being passed over highly electrified plates, the proportion of ozone in the whole being one part in 10,000,000. The air is driven by fans to the level of the bottom of the station, and two-thirds of it is distributed over the platform by ducts, with outlets at a height of 7 feet above the platform. The remainder is driven into the tunnel. The size of the pumping plant is such that it can be installed in a chamber 10 feet by 8 feet by 4 feet, and there are 2 miles of duct work.

BOOK REVIEWS.

Handbook of Alaska. By the UNITED STATES GEOLOGICAL SURVEY, Washington.

What may be termed the United States Geological Survey's "Handbook of Alaska" has just been issued in its seventh volume, summarizing for the year 1910 the conditions of the mining industry in our far north-west territory and the most important results accomplished by the investigations of its mineral wealth. The volume consists of 13 chapters, which are also published as separate pamphlets.

The separate reports are as follows:

The Mining Industry in 1910, by A. H. Brooks, 22 pages.

Geologic Features of Alaskan Metalliferous Lodes, by A. H. Brooks, 51 pages.

Mining in Southeastern Alaska, by Adolph Knopf, 9 pages.

The Eagle River Region, by Adolph Knopf, 9 pages.

The Upper Susitna and Chistochina Districts, by F. H. Moffit, 16 pages.

Preliminary Report on a Detailed Survey of Part of the Matanuska Coal Fields, by G. C. Martin, 11 pages.

A Reconnaissance of the Willow Creek Gold Region, by F. J. Katz, 14 pages.

Placer Mining in the Yukon-Tanana Region, by C. E. Ellsworth and G. L. Parker, 20 pages.

Water Supply of the Yukon-Tanana Region, 1910, by C. E. Ellsworth and G. L. Parker, 45 pages.

Mineral Resources of the Bonfield Region, by S. R. Capps, 18 pages.

Gold Placer Mining Developments in the Innoko-Iditarod Region, by A. G. Maddren, 35 pages.

The Shungnak Region, Kobuk Valley, by P. S. Smith and H. M. Eakin, 35 pages.

The Squirrel River Placers, by P. S. Smith, 13 pages.

Most of the reports are illustrated by sketch maps. Copies of any of the chapters may be had on ap-

plication to the Director of the United States Geological Survey, Washington, D. C.

The Paper Makers' Pocket Book. By JAMES BEVERIDGE. Second and enlarged edition. 211 pp. 59 pp. advertisements. D. Van Nostrand Company, New York. 1911. Price, \$2.00 net.

The second enlarged edition of "The Paper Makers' Pocket Book" is essentially, as the author indicates in the preface, a compilation of useful data for those interested in paper mill work and paper.

As the text was written in England, much of the data, such as cost, rates, etc., are based upon English practice and calculated upon the English system, and therefore do not necessarily apply to American conditions.

The book is divided into eight chapters and, aside from descriptive matter, contains much tabulated data as to the yield of pulp, paper testing, cost, trade customs, loading materials, colors, power consumption, analytical methods, etc.

The author has succeeded in producing a concise and valuable handbook which will appeal equally well to the paper chemist, engineer and office official.

O. KRESS.

Subject List of Works on Chemistry (Including Alchemy, Electrochemistry and Radioactivity) in the Library of the Patent Office. By W. TEMPLE FRANKS, Patent Office, London. Price, 6d.

This 12-month volume of 214 pages will be found particularly useful in building up trade and works libraries. Under each of the twenty-two divisions of chemistry are found enumerated the principal books and journal articles relating to the subject in question. Chemists and lawyers who have to do with patent cases will be able to obtain many hints from this book, in looking up their cases.

D. D. BEROLZHEIMER.

NEW PUBLICATIONS.

By D. D. BEROLZHEIMER, Librarian American Chemical Society.

- Chemistry, Inorganic—A Laboratory Manual of.** By E. C. BINGHAM AND GEORGE F. WHITE. 12mo., 147 pp. \$1.00. John Wiley & Sons, New York.
- Chemistry, Inorganic—.** By F. S. KIPPING AND W. H. PERKIN. (Two parts.) 8vo., 1210 pp. \$3.00. London, 1911.
- Chemistry, Medical and Toxicology—A Textbook of.** By JAMES W. HOLLAND. 3d Ed. 8vo., 655 pp. \$3.00. W. B. Saunders Co., Philadelphia.
- Chemistry, Organic—A Textbook of.** By A. F. HOLLEMAN. 9th Ed. L. 8vo., \$2.50. Leipzig, 1911. (German.)
- Casein, Its Preparation and Technical Utilization.** By ROBT. SCHERER. 2d Ed. 8vo. Scott, Greenwood and Co., London.
- Chemical Apparatus, Two Pieces of—.** By R. F. BACON AND P. B. DUNBAR. Circular No. 80, Bur. of Chemistry, Dept. of Agriculture.
- Chemistry, Colloid—, Introduction to.** By N. POESCHL. 3d Ed. 8vo., 80 pp. \$0.75. (Th. Steinkopff, Dresden.)
- Chemistry for Engineers and Manufacturers.** By B. BLOUNT AND A. BLOXAM. Vol. 2: Chemistry of Manufacturing Processes. 8vo., 530 pp. \$4.00. Chas. Griffin, London.
- Chemistry, Elements of Inorganic—.** By F. SWARTS. 8vo., 578 pp. \$4.25. (German.) Julius Springer, Berlin.
- Chemistry, Theoretical—, From the Standpoint of Avogadro's Rule and Thermodynamics.** By W. NERNST. 3d Ed. Roy. 8vo. \$4.50. London, 1911.
- Chicken Fat, Studies in—.** By M. E. PENNINGTON AND J. S. HEPBURN. Circular No. 75, Bur. of Chemistry, Dept. of Agriculture.
- Drugs, The Action of— Under Pathological Conditions.** By WM. SALANT. Circular No. 81, Bur. of Chemistry, Dept. of Agriculture.
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RECENT INVENTIONS.

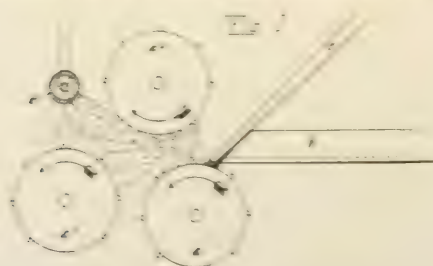
Reviewed by C. E. Parker, Supervisor of Chemical Experiments, Naval Post Office, Washington, D. C.

Manufacture of Cement from Furnace-Slag.

U. S. Patent No. 908,358.

This is a process for the manufacture of cement from liquid furnace slag or the like.

Referring to the accompanying illustrations the drum 1 has rotatably mounted thereon a second drum 2, and a third drum 3 is arranged above the drums 1 and 2. The glowing liquid slag is conducted to the drum 1 by a trough or channel 4, and the admixture is fed through a trough or channel 5 terminating near the circumference of the said drum. This drum pulverizes the material in the well known manner and throws part of it against



the drum 2 and part of it against the upper drum 3. The drums 2 and 3 rotate in the direction indicated in the drawing by the arrows so that the material on which they act is thrown from one to the other, and is in this manner very intimately mixed. The repeated impact of the material against the rapidly rotating drums causes it to be reduced to a fine state of pulverization, and owing to the fact that the ingredients are brought into most intimate contact with each other complete agglomeration results.

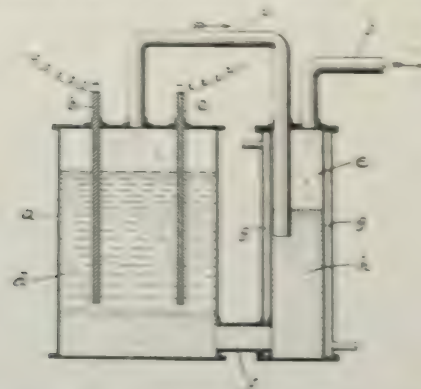
The inventor is Wilhelm Lossing, of Dresden, Germany.

Method of Producing Halogen-Oxygen Compounds by Electrolysis.

U. S. Patent No. 908,082.

This is an improvement in the method of producing halogen-oxygen compounds by electrolysis, which consists in allowing evolved chlorine gases to escape from the cell, absorbing the same in a liquid, which is not miscible with the electrolyte, and which absorbs and readily gives up the chlorine gas and returning the gas to the electrolyte.

The electrolyte is maintained at a constant level by adding to the neutral electrolyte a liquid which is not miscible with



one electrolyte but which readily dissolves chlorine. This liquid should be previously saturated with chlorine. The gases developed, particularly chlorine, are brought into intimate con-

tact with this liquid in such a manner that the gas does not escape and is absorbed and returned again to the electrolyte. The liquid or material used should be one which will absorb chlorine gas and readily give it up. Tetrachloride of carbon is a liquid which can be used and is especially suited for this purpose.

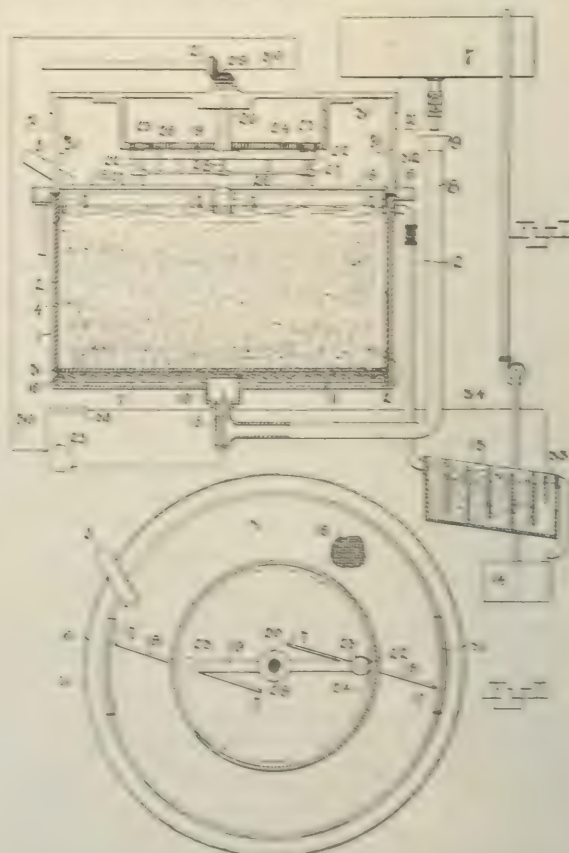
The inventor is Mathias Fort, of Schwanhausen, Germany, assignor to F. I. du Pont de Nemours Powder Company.

Apparatus for Electrochemical Treatment of Ores.

U. S. Patent No. 901,845.

This invention consists in apparatus for treating gold and other ores for the extraction of their metallic contents by means of an electric current operating in conjunction with a chemical solvent such as cyanide.

Transport is usually made for circulating the treatment liquid upwardly through the ore and through precipitation boxes. For this purpose there is provided a storage tank 7 from which liquid is delivered to a pipe 8, the mouth 9 of which is raised above the tank. The pipe 8 connects with a chamber, 10, in the bottom of the tank, from which a number of perforated distribution pipes, 11, radiate under the filter 12. Near the top of the vat or a float-off pipe, 13, conducts the liquid to the



precipitation boxes 11 after passing which flows to a sump, 14, and is pumped back to tank 7.

The current is passed through the ore in the same direction as the liquid, or in other words the anode is placed at the bottom of the vat and the cathodes at the top. The anode 15 is shown positioned in chamber 10, beneath the filter 12 and supporting the same is a heavy metallic netting 16 which bears a set of supplementary anode for distributing the current over the ore.

The cathode, marked 17 and several in number, are arranged at the top of the vat to dip into surfaces of the liquid. They are carried upon the extremities of arms 18 having a planetary motion with respect to the axis of the vat. Such motion causes the cathodes in course of time to traverse the entire surface of the liquid and thus cause the current to penetrate every part of the body of ore and act upon every particle of metal therein.

The return circuit from the cathodes to the source of current 25 is made by means of springs or brushes, 26, suspended below the arms of the spider 19 and resting upon rings, 27, upon the spindles 22. These springs or brushes connect with a rod, 28, passing up the center of shaft 20 and making rubbing contact at 29 with the return conductor 30. The whole of the cathode mechanism is carried in a frame, 31, which is supported by an insulating medium, 32, upon the vat 1.

In order to assist precipitation upon the zinc in the boxes 13, a cathode, 33, may be suspended in the discharge end of each box. A portion of the current thus passes through the liquid flowing off by pipe 12 and through the boxes 13, returning to the dynamo through a conductor, 34, in which a resistance, 35, may be inserted to regulate the amount of the diverted current.

The inventor is Tullio Bubala, of Indianapolis, Indiana.

Process of Obtaining Nitrogen.

U. S. Patent No. 999,003.

This invention relates to the production of nitrogen from atmospheric air and specifically to processes for removing oxygen from air in such manner as to leave the residual nitrogen in condition for use in the manufacture of nitrogen compounds, particularly cyanids, which require nitrogen.

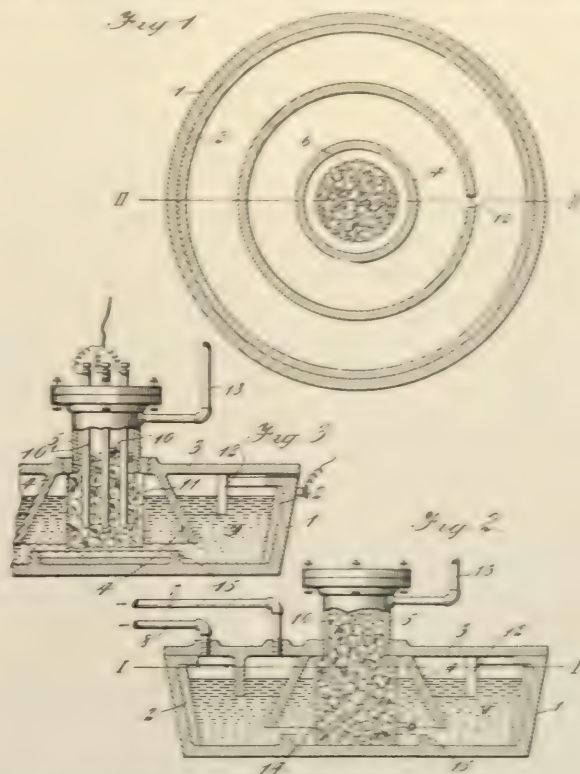
The method consists in bringing air—previously deprived of all moisture and carbon dioxide—into contact with molten sodium or potassium cyanid, or a mixture thereof, at a temperature of 500° C. or over, whereupon the oxygen of the air will react with a portion of the cyanid, *e. g.*, sodium cyanid to form sodium cyanate which, being perfectly miscible with the cyanid, will diffuse throughout the molten mass, while the nitrogen content of the air will remain unaffected and may be collected in the pure state. The cyanate is also of substantially the same density as the cyanid.

The sodium cyanate contained in the molten cyanid may be continuously or intermittently reduced to sodium cyanid as it accumulates above a certain percentage in the mass, by means of certain metals, and also by carbon. The metal, *e. g.*, iron, combines with the oxygen of the cyanate to form iron oxid which contaminates the cyanid, but will settle to the bottom of the molten mass if undisturbed. The iron does not begin to reduce the cyanate until the latter constitutes about 10 per cent. or more of the molten mixture and it will continuously reduce any cyanate which may be formed in the mixture in excess of this approximate percentage. Zinc will also continuously reduce the cyanate which may tend to accumulate above a certain percentage (not determined) in the molten cyanid. The zinc oxid may be separated by settling and collected for use as such.

Carbon easily reduces the cyanate and forms a gaseous oxid

which removes itself entirely and continuously from the molten cyanid and does not contaminate it.

Coal may be used as the source of carbon, the impurities so introduced, to wit, the ash in the coal, not being particularly objectionable. If, therefore, air be injected into or passed over the surface of a body of molten sodium cyanid contained



in a suitable metal retort which also contains lumps of unthracite coal submerged in the cyanid, the oxygen of such air will combine with some of the molten cyanid to form sodium cyanate, which will diffuse in the cyanid, and come into contact with the coal, which will promptly reconvert it into sodium cyanid with evolution of carbon monoxid gas:



If the reduction be effected in an ordinary pot or retort, the carbon monoxid will rise through the melt and mix with the residual nitrogen of the air so that the product will be worthless.

One object of the process is to continuously or intermittently remove the oxygen from the air by means of molten cyanid, and to continuously or intermittently reduce the resultant cyanate by means of coal in such manner that the carbon monoxid does not come into contact nor mix with the nitrogen, which may, therefore, be obtained pure.

Forms of apparatus which may be used for this purpose are shown in the accompanying illustrations.

The Inventor is Charles E. Acker, of Ossining, New York, Assignor to the Nitrogen Company, of New York.

MARKET REPORT.

(AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF OCTOBER.)

For Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

ORGANIC CHEMICALS.

Acetanilid.....Lb.	20 ¹ / ₂ @	23
Acetone (drums).....Lb.	13 ⁵ / ₈ @	15 ² / ₃
Alcohol, grain (188 proof).....Gal.	2.56 @	2.58
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	3.15 @	3.25
Acetic Acid.....C.	1.69 @	2.39
Aniline Oil.....Lb.	11 ¹ / ₂ @	11 ⁵ / ₈
Benzoic Acid.....Oz.	11 ¹ / ₄ @	12
Carbon Tetrachloride (drums).....Lb.	7 ³ / ₄ @	8 ¹ / ₄
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	35
Carbolic Acid (drums).....Lb.	15 @	15 ¹ / ₂
Citric Acid (domestic).....Lb.	38 ¹ / ₂ @	39
Camphor (refined in bulk).....Lb.		44 ¹ / ₂
Dextrine (imported potato).....Lb.	6 @	7 ¹ / ₆
Dextrine (corn).....C.	2.84 ¹ / ₂ @	3.00 ¹ / ₂
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 ¹ / ₂ @	9 ¹ / ₂
Glycerine (dynamite).....Lb.	17 @	17 ¹ / ₃
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7 @	7 ³ / ₈
Pyrogalllic Acid (bulk).....Lb.	1.25 @	1.55
Salicylic Acid.....Lb.	31 ¹ / ₂ @	33 ¹ / ₂
Starch (corn).....C.	2.12 ¹ / ₂ @	2.28 ¹ / ₂
Starch (potato).....Lb.	4 @	4 ¹ / ₄
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 ⁷ / ₈ @	5 ¹ / ₄
Tannic Acid (regular in bulk).....Lb.	48 @	50
Tartaric Acid, crystals.....Lb.	30 ¹ / ₄ @	30 ³ / ₄

INORGANIC CHEMICALS.

Acetate of Lime (gray).....C.	1.87 ¹ / ₂ @	1.92 ¹ / ₂
Acetate of Lead (brown, broken).....Lb.	7 ³ / ₄ @	8
Alum (lump).....C.	1.75 @	2.00
Aqua Ammonia (drums) 16°.....Lb.	2 ¹ / ₂ @	2 ¹ / ₂
Ammonium Chloride, gray.....Lb.	6 @	6 ¹ / ₄
Arsenic, white.....Lb.	2 ¹ / ₄ @	3
Ammonium Carbonate, domestic.....Lb.	8 @	8 ³ / ₈
Aluminum Sulphate.....Lb.	90 @	1 ³ / ₄
Ammonium Vanadate.....Oz.	41 @	50
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 ¹ / ₄
Barium Nitrate.....Lb.	5 ¹ / ₂ @	6 ¹ / ₄
Borax, crystals (bags).....Lb.	3 ¹ / ₂ @	4
Boric Acid, crystals.....Lb.	7 @	7 ¹ / ₂
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.27 ¹ / ₂ @	1.37 ¹ / ₂
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	94 @	96
Chalk (light precipitated).....Lb.	4 ¹ / ₂ @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (bags).....C.	60 @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.75
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 @	8 ¹ / ₂
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	85 @	88
Nitric Acid, 36°.....Lb.	3 ⁵ / ₈ @	4 ¹ / ₂
Nitric Acid, 42°.....Lb.	4 ⁷ / ₈ @	5 ¹ / ₄
Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25

Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 ³ / ₈ @	10 ³ / ₄
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals.....Lb.	8 ¹ / ₄ @	9 ¹ / ₂
Potassium Nitrate (crude).....Lb.	4 ¹ / ₈ @	4 ⁷ / ₈
Potassium Bichromate, 50°.....Lb.	7 ³ / ₈ @	7 ³ / ₄
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	63 ¹ / ₂ @	65 ¹ / ₂
Salt Cake (glass-makers).....Lb.	57 ¹ / ₂ @	67 ¹ / ₂
Silver Nitrate.....Oz.	33 ³ / ₄ @	35 ⁵ / ₆
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 @	4 ¹ / ₂
Sodium Chlorate.....Lb.	8 ¹ / ₄ @	9 ¹ / ₂
Sodium Bicarbonate (English).....Lb.	2 ³ / ₄ @	3
Sodium Bichromate.....Lb.	5 ⁵ / ₈ @	5 ⁷ / ₄
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 ¹ / ₂
Sodium Hydroxide, 60 per cent.....C.	1.80 @	1.85
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate.....Lb.		8
Sodium Nitrate, 95 per cent., spot.....C.	2.22 ¹ / ₂ @	2.27 ¹ / ₂
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 ³ / ₄ @	10
Strontium Nitrate.....Lb.	7 ¹ / ₄ @	8
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	85 @	1.00
Talc (American).....Ton	15.00 @	20.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	11 ¹ / ₂ @	12 ¹ / ₄
Tin Oxide.....Lb.	45 @	47
Tin Chloride (36°).....Lb.	11 @	11 ¹ / ₂
Zinc Chloride (granulated).....Lb.	4 ¹ / ₂ @	4 ¹ / ₂
Zinc Sulphate.....Lb.	2 ¹ / ₄ @	2 ¹ / ₂

OILS, WAXES, ETC.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 ¹ / ₂
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	9 @	20
Corn Oil.....C.	6.32 ¹ / ₂ @	6.37 ¹ / ₂
Cottonseed Oil (crude), f. o. b. mill.....Gal.	32 @	32 ¹ / ₂
Cylinder Oil (light, filtered).....Gal.	19 ¹ / ₂ @	20
Japan Wax.....Lb.	8 ¹ / ₄ @	9
Lard Oil (prime winter).....Gal.	82 @	85
Linseed Oil (double-boiled).....Gal.	93 @	94
Paraffine Oil (high viscosity).....Gal.	23 ¹ / ₂ @	24
Paraffine (crude 120 @ 122 m. p.).....Lb.	3 @	3 ¹ / ₈
Paraffine (refined, domestic) 120 @ 122 m. p.....Lb.	4 ¹ / ₂ @	4 ³ / ₄
Rosin Oil (first run).....Gal.	38 ¹ / ₂ @	50
Spindle Oil, No. 1.....Gal.	14 @	14 ¹ / ₂
Stearic Acid (double-pressed).....Lb.	10 ¹ / ₄ @	10 ¹ / ₂
Sperm Oil (bleached winter) 38°.....Gal.	76 @	78
Tallow (acidless).....Gal.	63 @	65
Tar Oil (distilled).....Gal.	30 @	31

METALS.

Aluminum [No. 1 ingots].....Lb.	18 ¹ / ₂ @	19
Antimony (Hallet's).....Lb.	7.50 @	7.75
Bismuth (London).....Lb.	— @	1.80
Copper (electrolytic).....Lb.	12.25 @	12.35
Copper (lake).....Lb.	12 ¹ / ₂ @	12 ⁵ / ₈
Lead, N. Y.....Lb.	4.20 @	4.25
Nickel.....Lb.	40 @	50
Platinum (refined).....Oz.	46.00 @	46.50
Silver.....Oz.	54 @	54 ¹ / ₂
Tin.....Lb.	— @	42
Zinc.....Lb.	5.95 @	6.10

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EDITORIALS

PROFESSIONAL ETIQUETTE.

At a time when our Society is endeavoring to obtain from the Federal, State and Municipal Governments that recognition to which it is entitled by virtue of its aims, its size and the representative men of science who are included in its membership, it seems most desirable and necessary that some consideration be given the subject of Professional Etiquette. An early discussion of this subject appears to be almost mandatory if the public at large is to place in a chemist's opinion that confidence which it now places in the opinions of physicians and lawyers. The two last-named professions are held up to a certain standard by the State Examining Boards for law and medicine, and this preliminary process of elimination is in a certain sense followed up by the supervision of various county medical societies and bar associations. It may be that we will in the future have state examinations for food chemists, sanitary chemists and municipal chemists, but at this writing there is nothing that will assure the layman that a certain man has enjoyed that necessary education which properly fits him for making accurate analyses and rendering opinions on matters involving chemical principles. At the present time it quite frequently happens that a manufacturer submits a commercial product to "one chemist after another" until he has three or more entirely different reports on the same article. It is this very fact, which is undermining the reputation of the chemical profession at large, and the importance of the subject warrants a careful consideration of the conditions.

About one year ago a specimen of bleached cotton was handed to the writer with the request that it be examined for chlorin. On returning a negative report, the bleacher stated that two other chemists had each found chlorin in the goods. A careful

"following up" of the case showed that the two former chemists had examined for chlorides while the third chemist had examined for free chlorin which in this case was the only form of chlorin in which the bleacher was interested and which might prove dangerous. Thus it is seen that *incomplete* reports are as dangerous as careless analyses. Aside from these questions which involve foresight, accuracy and perspective, we have many of us experienced public criticism (by chemists) of the work of other chemists. This has been resorted to, probably because the critic saw no other way of having a careless or less experienced colleague brought to task for having injured the standing of his profession. This in turn suggests to our minds the necessity of a Supervisory Board as a part of our American Chemical Society: a Board whose duty it shall be to hear complaints of members in cases involving a breach of professional etiquette or cases where the quality of the work done by a member reflects on the reputation of chemists as a *professional* body. Our Society should in no wise seek to dictate to the schools where a man obtains his chemical education but it should endeavor to define rather clearly the term "chemist," so that a manufacturer when seeking the advice of a chemist may obtain from the office of the American Chemical Society the name of a qualified chemist in any one of the important cities of our Country. If found advisable this list might be subdivided under such headings as Analysts, Engineering Chemists, Consulting Chemists (inorganic), Consulting Chemists (organic), etc.

Very recently the following incident was brought to the attention of the writer: "A," who is a consulting chemist, gave to "B," an analyst, and to "C," an analyst (both of these being reputable analytical chemists), a certain material which was to be examined qualitatively for the presence of arsenic. "B" re-

ported that arsenic was absent while "C" reported the presence of a *considerable* amount of arsenic. "C" was corroborated in his report by "D" (another analyst). What credence is to be given the report of "B"? If "B's" methods are faulty, what is to warn a manufacturer of this fact? What redress has "A" if the report of "C" and "D" should prove inaccurate and needless anxiety has been caused by this fact?

To conclude, if the title of chemist, analyst, and so on, is given by the American Chemical Society to those of its members who possess definite qualifications, the manufacturers of our Country will cease to remark that "chemists are bluffers" as one gentleman recently put it in a private conversation. In other words, it is a *pleasure* to have one's name recorded as a member of our Society, but it should be an *honor* to be recognized as a qualified consulting chemist or analyst by the American Chemical Society.

FREDERIC DANNERTH.

THE POTASH SUPPLY.

There will always be a "potash situation" and the possibility of a controversy so long as the world's supply of potash happens to be lodged in one country and is controlled by a monopolistic combine of which the government of the country in question through its ownership of mines is a part. At the bottom of the recent and present controversy between the American consumers of potash and the German producers stands the fundamental fact that we are forced to buy our potash of Germany because there is no other source of supply. Germany can charge all that the trade will stand, for her potash, in defiance of any natural laws of supply and demand and Americans will have to pay the price.

The general situation has changed but little during the year and indeed not much change was expected after the failure of our government to reach a successful conclusion in its diplomatic negotiations. The American contractors, who arranged for the delivery of their requirements through an American concern which had in turn contracted with the independent mines, are paying syndicate prices for their deliveries, although the money is paid under protest on account of the sur-tax, and it is possible that some settlement will later be arrived at.

The great hope of American consumers lies in the discovery of adequate potash deposits in the United States. The government has wisely appropriated a sum of money, for the purpose of prospecting and investigating probable sources of supply. Recently announcement has been made by the Secretary of Agriculture that potash has been discovered in the West in large quantities, but details are withheld until the assembling of the next Congress, when they will be communicated to the legislative committees which have the matter in charge. It is to be hoped that this important announcement will be fully supported by the facts when they are made known and that the deposits will prove commercially available in the near future. No other influence, it would seem, can change the monopolistic German attitude.

The German Syndicate is already greatly interested in Secretary Wilson's announcement, and it has been pointed out in the newspapers that even if potash were obtainable in the Western States, it could not compete with German potash on account of high freight rates. Statements have also been made to the effect that before the Syndicate was formed, an examination was made of possible American potash deposits, and the conclusion was reached that America possessed no deposits large enough to be worked at a profit.

Feldspar and other potash silicates as sources of soluble potash do not appear to be arousing interest in the fertilizer trade or chemical manufacture. The processes which have been proposed—fusion with common salt or with salt and lime, electrolysis, etc.—do not give promise of profitable working. The proposition is a very low-grade one at best. The best potash silicates carry only 12–14% of actual K_2O , and with the addition of fluxes these percentages would be still further reduced. Lixiviation and concentration would probably prove far too expensive, considering the price of the finished product. Soluble potash from insoluble silicates does not appear to be in the realm of the possible at the present time.

The only hope lies in the discovery of soluble sources of supply, and it is for this reason that the fertilizer and chemical manufacturers as well as the general public are awaiting with the greatest interest further announcements from the Department of Agriculture.

W. D. RICHARDSON.

ORIGINAL PAPERS.

THE PREPARATION AND PROPERTIES OF METALLIC CERIUM.*

By ALCAN HIRSCH.

INTRODUCTION.

In view of the amount of research¹ on the rare-earths, it is remarkable that little has been done on the metals themselves. This is easily understood, however, when one considers the scarcity of pure

material to work with and the difficulty of reducing these very electropositive elements from their compounds. What metal has been obtained has been, in most cases at least, small in amount and very impure, usually contaminated with the other members of the group. On account of the rarity of the materials to work with, little has been done in a study of the physical and chemical properties of these rare-earth metals, and the field of alloys has been almost untouched.

* A paper presented at the Twentieth General Meeting of the American Electrochemical Society, Toronto, Canada, September, 1911.

In the present research, cerium, the leading member of the cerium group, was chosen as the rare-earth element to be studied. The investigation was undertaken with a two-fold purpose. First, starting from as pure cerium salt as it was possible to obtain, it was desired to prepare the metal in quantities sufficiently large that its physical and chemical properties could be studied and a large number of alloys could be made. Second, by preparing metal from the unpurified rare-earth residues from monazite sand, obtained as a by-product in the incandescent gas-mantle industry, it was hoped that alloys of commercial value could be obtained. In other words, whereas the application of these residues as oxalates or oxides is very limited to-day, their value might possibly be increased materially if a useful metallic or alloyed product be prepared from them.

The writer gratefully acknowledges his indebtedness to Mr. H. S. Miner, chief chemist of the Welsbach Light Company, for his very generous supply of pure rare-earth salts and rare-earth residues, and to Professors Burgess and Lenher, of the University of Wisconsin, for the facilities of their laboratories and their helpful advice and encouragement during the progress of this research. The electrolytic work was done in the laboratories of Applied Electrochemistry, while the analyses and the chemical preparations were made in the Department of Inorganic Chemistry.

This research was begun in December, 1907, and concluded June, 1911. The actual time devoted to this study covered a period of over three years.

HISTORICAL.

In 1751 Cronstedt² discovered the mineral cerite in a mine of Bastnaës. In 1784 Bergmann and d'Elhyar³ confused the rare-earth with lime, and published an incorrect analysis of this mineral cerite. In 1794 Gadolin⁴ discovered the rare-earths in a heavy black mineral, afterwards called gadolinite.

In 1804 cerium was discovered simultaneously by Klaproth⁵ in Germany and by Berzelius and Hisinger⁶ in Sweden. The first investigator named the oxide ochre earth because of its color, but Berzelius and Hisinger called the new element cerium, after the planet Ceres. About the same time Vauquelin⁷ confirmed the discovery of a new earth by analyzing cerite, and then undertook the study of the salts of cerium.⁸ In 1814 Berzelius and Galin⁹ separated the oxides of cerium and yttrium. Between this period and that of the famous researches of Mosander, numerous articles were published on cerium and the minerals in which it was found, but the material used was necessarily very impure, and what was called at that time cerium oxide was in reality the mixed oxides of the cerium group.

In 1839 Mosander¹⁰⁻¹¹ announced that cerium oxide was a mixture of two oxides, those of cerium and lanthanum. In 1841 he stated that cerium oxide contained still another oxide, that of didymium. In 1868 Wolf¹² determined the equivalence of cerium and announced that the so-called cerium compounds were mixtures of two or more rare-earth elements.

In 1879 Lecoq de Boisbaudran,¹³ while examining the didymia obtained from the mineral samarskite, isolated a new element which he called samarium. In 1885 Auer von Welsbach¹⁴ showed that didymia was a mixture of the oxides of two new rare-earth elements, neodymium and praseodymium.

At the present time there are about 15 well identified elements which, for chemical reasons, among other properties that of the insolubility of their oxalates in slightly acid solution, are classified as rare-earths. These rare-earths are usually subdivided into three groups in the order of their basicity—the cerium group, the gadolinium group and the yttrium group. There is no absolute differentiation of one group from another, but rather a gradual transition. Usually only the five elements—cerium, lanthanum, neodymium, praseodymium and samarium—are included in the cerium group.

The present research is concerned with the cerium group, and principally with cerium itself. But in the rare-earths relations between members of the same group are much closer than among other kindred elements, as the platinum metals. For example, the atomic weights of lanthanum, cerium and praseodymium are, respectively, 139, 140.25 and 140.6; therefore the chemistry of one element concerns that of the other members of the group—to a certain degree at least.

Previous Work on the Rare-earth Metals.

Two general methods of preparation have been used for the production of the rare-earth metals:

1. Reduction of the oxide or chloride by one of the very electropositive metals.
2. Electrolysis of a fused salt.

Mosander and Marignac¹⁵ appear to have been the first to produce metallic cerium by a thermal reduction using the alkali metals. Wöhler¹⁶ describes the difficulty of the reduction using sodium metal and cerium chloride, and states that 12 grams of sodium yielded only 50–60 milligrams of cerium metal. Winckler¹⁷ used metallic magnesium and cerium dioxide and obtained a pyrophoric mixture. Recently some attempts have been made to produce the metals by improved methods of thermal reduction. Matignon¹⁸ used metallic aluminum and magnesium, and Schiffer,¹⁹ in Muthmann's laboratory, experimented with the reduction of the oxides by aluminum. From the writer's own experiences in the attempted thermal reduction of these oxides, which is described further on in this article, it appears that the reduction yields either a lower oxide, an impure mixture of partially reduced metal and oxide, or an alloy of the reduced metal and rare metal, such as an aluminum-cerium alloy.

In 1874 Frey²⁰ published a notice of the preparation of the rare-earth metals in the laboratory of Dr. Schuchardt, in Gorlitz, using the electrolytic method of Bunsen. The following year Hillebrand and Norton²¹ published an account of their work on the electrolysis of the fused chlorides of cerium and potassium. They succeeded in producing about six grams of

cerium. In 1895 Pettersson²² attempted to electrolyze the oxides, but produced only the carbides. In 1902 Muthmann²³ and his associates published the first of a very comprehensive series of articles²⁴ on the metals of the cerium group. Besides preparing the metals of the cerium group, they devised a new type of electrolytic vessel which they found useful in their method of electrolysis. They have also prepared an alloy which they call "mischmetall," which is an alloy of the cerium-yttrium group metals. Borchers and Stockem²⁵ have devised a method in which they use the double cerium-calcium chlorides, and have patented this process (German Patent 172,529). The above-mentioned electrolytic methods will be referred to again further on in this article.

PREPARATION OF MATERIAL.

The general scheme followed in this research was to use the mixed rare-earth oxides for experimenting on the exact conditions required for the preparation of the desired salt and, after the proper conditions of the process had been determined, to prepare the pure cerium salt. Oxalates of the rare-earths, a by-product of the commercial extraction of thorium and cerium from monazite sand, were employed for these experiments. The oxides, prepared by calcining the oxalates at a temperature of 750–800° C. in a gas muffle furnace, analyzed 97.8 per cent. rare-earth oxides, of which approximately 49 per cent. was cerium dioxide. They dissolved completely in nitric acid, and also in hot concentrated hydrochloric acid on digestion, which is usually taken as a check that the cerium content is less than 50 per cent.²⁶

Preparation of Anhydrous Chlorides.

The first salts required were the anhydrous chlorides (composition RCl_3). There are several hydrated chlorides of cerium known, of the compositions: $2\text{CeCl}_3 \cdot 15\text{H}_2\text{O}$; $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$; $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$; $\text{CeCl}_3 \cdot \text{H}_2\text{O}$. Cerium chloride is similar to magnesium chloride in that when its solution is evaporated to dryness and calcined, HCl is evolved with partial decomposition of the chloride to oxychloride and oxide.

A good many methods have been proposed for the preparation of anhydrous or dehydrated chlorides of cerium, among which may be mentioned the following: Heat the hydrated chlorides with NH_4Cl until the latter salt is completely volatilized.²⁷ Behringer²⁸ heated the hydrated chlorides with NH_4Cl in a glass tube in a current of chlorine. Robinson²⁹ heated the oxalates to a temperature of about 130° in dry HCl gas until all of the oxalic acid had sublimed, then gradually raised the temperature to a red heat. Didier³⁰ heated CeO_2 in a current of CO_2 and chlorine. Muthmann and Stutzel³¹ passed H_2S over anhydrous sulphate heated to a high temperature, and then a mixture of CO_2 and dry hydrochloric acid gas. Mosander³² burned cerium in chlorine. Moissan³³ attacked the carbide by hydrochloric acid gas at 650° or chlorine at 250°. Meyer³⁴ converted the oxides to chlorides by vapors of CCl_4 .

A number of methods for the preparation of the anhydrous chlorides were tried before a suitable

one was found. The large quantity of chloride which was required (several kilograms) necessitated that the preparation should be done in as simple and rapid a manner as was possible. Both aqueous and non-aqueous methods were tried, and below are given the different processes experimented with and their relative advantages and disadvantages.

One of the best methods for the preparation of this type of chlorides (those that decompose on evaporation and calcination from aqueous solution) is to heat the hydrated chloride with NH_4Cl . In the case of cerium chloride, Muthmann³⁵ describes in some detail this method, and mentions the tediousness and care required. To prepare a kilogram or so may require several days' work to effect the dehydration. The use of a platinum finger crucible is recommended, and not more than 50 grams of the hydrated cerium-ammonium chloride should be heated at a time. The heating must be done very cautiously or the product will be contaminated with oxychloride or oxide. The writer has tested thoroughly this method, and finds it very poor in this case for large scale operations. One set of experiments which was tried will illustrate the difficulties encountered. Two kilograms of the mixed oxides were dissolved in 4 liters HCl (22° Bé.) and about 4½ kilograms NH_4Cl were added. Evaporation was carried to dryness in large (35 cm.) porcelain evaporating dishes. About a kilogram of the chlorides was introduced into a large Dixon crucible, which was heated in a gas crucible furnace at a low temperature until the white fumes of NH_4Cl came off copiously. The fumes were conducted out of the window by a suitable flue, and the atmosphere within the furnace was at all times a reducing one. The heating was continued until the contents of the crucible were molten and white fumes ceased to come off. A strong odor of HCl gas and chlorine was noticed toward the end of the operation. The product did not melt to a clear liquid as the properly prepared anhydrous chloride does, but fused to a slimy mass. Analysis showed that the chloride was highly contaminated with oxide, and although 1,100 grams were obtained, the product was unsuitable for electrolysis.

Borchers and Stockem³⁶ state that many of the difficulties encountered in the dehydration of hydrated cerium chloride can be avoided by the preparation of the double calcium-cerium chloride, and that this salt can be prepared in the anhydrous state without decomposition by simple calcination. These results could not be duplicated by the writer. Forty-seven grams of the hydrated chloride of cerium were dissolved to a clear solution in water slightly acidified with HCl , and 15 grams of CaCl_2 were added. The solution was evaporated to dryness and calcined. The salt which was obtained did not melt to a clear solution, and was unsuited for electrolysis.

Dennis and Magee³⁷ have prepared the hydrated chloride $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, which loses water in a vacuum or over dehydrating agents, whereas the hydrate $2\text{CeCl}_3 \cdot 15\text{H}_2\text{O}$ does not effloresce when placed over sulphuric acid.³⁸ It was thought that perhaps the

anhydrous chloride could be prepared from the hydrated salt $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. The concentrated solution of the chlorides, prepared by the action of concentrated HCl on the mixed oxides, was cooled to 0°C . by ice, and dry HCl gas was passed into the solution. After a time crystals began to separate out. They were filtered, dried in the air, and the chlorine content determined by titration with standard AgNO_3 . The per cent. of chlorine was found to be 26.6 per cent., whereas that in $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ is 28.6 per cent. The presence of rare-earths other than cerium probably caused the difference in composition. When this salt was heated in a partial vacuum (water-pump) at 100° for two hours, the loss in weight was 4.4 per cent. When dried over P_2O_5 in a vacuum desiccator for several days, the loss in weight was about 8 per cent. The salt $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was then dehydrated in dry HCl gas. Small quantities of the salt were placed in several porcelain boats in a porcelain tube furnace through which dry HCl gas was passed. The maximum temperature in the tube was 210° , and the average temperature was 195° . The product in the boat placed in the center of the tube lost 35 per cent. in weight, and analysis showed a chlorine content of 39.3 per cent. The chlorine content of the anhydrous chloride CeCl_3 is 43.2 per cent. The chloride so prepared melts to a clear liquid. Attempts were then made to prepare the anhydrous chloride on a larger scale by this method: 1,500 grams of the mixed oxides were converted into chlorides, and then the hydrate $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ was prepared by the method of Dennis and Magee, described above. The yield of salt was very small, and the operation is a difficult one to perform on a large scale, due to the fact that a low temperature is necessary and the absorption of HCl gas in water is accompanied by a considerable evolution of heat. Moreover, a simple method was found for preparing the monohydrate, and as the dehydration of the septa-hydrate passes through the stage of the monohydrate, this method was abandoned.

As the dehydration of the chlorides appear to be the principal difficulty in the preparation of the anhydrous chlorides, it was thought that a suitable process might be developed by the use of non-aqueous solvents. As the action of non-aqueous solvents was found to be somewhat slower than the action of aqueous ones on cerium compounds, it was desirable that a readily decomposable substance be used as the starting material, and the rare-earth carbides were chosen for this reason.

The carbide* RC_2 was prepared by heating the

* Moissan (*C. R.*, **124**, 1235) states that pure CeO_2 (free from iron and other earths) may be prepared from cerium carbide by fractional treatment of the carbides with dilute HNO_3 . A modification of this method for the preparation of cerium dioxide free from the other rare-earths was made as follows: 100 grams of the mixed rare-earth carbides were ground to a fine powder and were treated with a small amount of dilute HNO_3 . After the second treatment iron could not be detected in the residue by the sulphocyanide test. A larger amount of dilute HNO_3 was added and the solution after filtration was treated by Mosander's method. (Chlorine passed into the solution which had been made alkaline with KOH.) The precipitate after washing showed only a very faint absorption spectrum. For rapid preparation of cerium dioxide this method appears to be very good. The oxide prepared by this means is yellow when calcined at 100° , but turns darker when heated to 1000° .

mixed oxides with powdered graphite in an arc furnace. Several kilograms of this material were prepared according to the method of Moissan.³⁹ The proper mixture to be heated was found to be 500 parts mixed oxides and 132 parts finest graphite powder. When a graphite crucible was used as one terminal and a graphite rod (about 1 inch diameter) as the other, the carbide was easily prepared on a large scale by using a 25 kw. arc (AC or DC). Care should be taken to protect the eyes properly as the rays emitted from the hot mass are especially harmful as they contain a certain amount of ultra-violet rays.

Alcoholic HCl,† made by passing dry HCl gas into cooled absolute alcohol, acts readily on the carbides. The solution of the chlorides prepared by this method always contains more or less graphite, and is very difficult to filter because of its viscosity. By evaporation to dryness, the anhydrous chlorides are obtained, but care must be taken to prevent absorption of moisture, as the syrupy liquid is extremely hygroscopic. Several minor difficulties are encountered in this method, the principal ones being the solubility of acetylene in absolute alcohol (6 times as soluble as in water) and the lesser solubility of the chlorides in absolute alcohol (one-third as soluble as in water). Because of the above disadvantages, and the expense involved in the use of absolute alcohol and its subsequent loss on evaporation, this method was not suitable to large scale operations. The action of HCl gas and chlorine on the carbides gives chlorides which are highly contaminated with carbon and are therefore useless for electrolytic purposes, as carbon in a finely divided state with the chlorides will form carbides on electrolysis.

In view of the fact that the non-aqueous methods were not suitable for the problem at hand, resort was again made to dehydration methods. It was found that by treating the mixed oxides with concentrated HCl, evaporating to dryness, adding more HCl and repeating the process a number of times, a product was obtained corresponding to one of the lower hydrates of the chlorides. This white solid was very hygroscopic, and dissolved in water with avidity and evolution of considerable heat; when broken into lumps and calcined at a low temperature (not exceeding 125°) on an asbestos-covered hot plate further dehydration occurs without decomposition. The heating should be continued for a long time (about 12 hours), and the temperature must be kept low. If these directions are followed, a product corresponding approximately to the monohydrate is obtained. The great difficulty is to get rid of the last molecule of water, which is the most tightly bound of all, without decomposing the chlorides.

Matignon⁴⁰ and Bourion⁴¹ have done a great deal of work on the preparation of anhydrous chlorides. They have found that certain chlorides of the metalloids, especially those of phosphorus and sulphur, act as catalyzers in the dehydration of hydrated

† Meyer and Kess (*Ber.*, **35**, 2622) have used alcoholic HCl for the preparation of cerium salts. They found that this solvent has no action on the oxides but reacts readily with the carbonates. They did not use the carbide.

chlorides, and that in the presence of dry HCl gas, chlorine and sulphur monochlorides (S_2Cl_2) the chlorides of silicon, aluminum, thorium, neodymium, praseodymium, samarium and vanadium can be prepared in the anhydrous condition.

For the problem at hand this method had apparently many advantages and few disadvantages, chief of which was the very disagreeable nature of sulphur monochloride. It was resolved, therefore, to try out this method on the preparation of the anhydrous mixed chlorides. About 400 grams of the hydrated chlorides were placed in a porcelain tube furnace through which was passed a mixture of chlorine, S_2Cl_2 , and HCl gases. The maximum temperature was about 300° , and the heating was continued for two and one-half hours. The product in the center of the tube was fritted together, and a sample for analysis was taken from this portion; 1.4 per cent. was insoluble, and the chlorine content of the soluble part was 42.4 per cent.—the per cent. of chlorine in $CeCl_3$ is 43.2 per cent. The product melted satisfactorily, and the method seemed suitable, so that a plan was devised for its application on a larger scale.

A terra-cotta drain pipe, four inches (10 cm.) in diameter and four feet (1.2 m.) in length, was fitted at both ends with graphite caps, through which passed short pieces of glass tubing, two at one end and one at the other. The furnace was a circular-flame tube furnace in which the pipe could be heated gradually and uniformly, and the temperature was under positive control. The monohydrated chlorides, prepared by the method previously described, were dehydrated, about a kilogram at a time. The salt was spread evenly in the pipe, in a layer about $\frac{3}{4}$ inch (2 cm.) thick. The caps were then inserted and the ends heavily luted with a mixture of magnesia, asbestos fiber, cement, fire-clay and water, and allowed to dry, when a joint practically gas-tight was obtained. Dry HCl gas was passed over the chlorides and as soon as the air was displaced the heating was commenced with a small smoky flame. After the tube was warm, chlorine and S_2Cl_2 vapors, as well as dry HCl, were passed through the tube and the temperature was gradually raised to just below 400° . The dehydration is completed in about three hours if the temperature is correctly adjusted, but may take longer. The anhydrous chlorides are placed, while still warm, in dry bottles, and the corks paraffined in. Care must be taken to prevent the sewer-pipe from cracking when being heated, and this tendency forms one of the principal weaknesses of the process. A metallic container can not be used in the dehydration on account of the highly corrosive action of the vapors.

The sulphur monochloride seems to catalyze the dehydration process, and has the further function, together with the chlorine gas, of reconverting to chloride any oxide or oxychloride which may form. If the temperature is too high, oxide or oxychloride may form even in the presence of chlorine and sulphur monochloride. The dehydration may be carried out by HCl gas alone, and a scheme was devised for

preparing pure anhydrous cerium chloride using this method. Since the process was the outcome of much work and of experience in the handling of the chlorides, it is described here in some detail.

The double cerium ammonium nitrate from the fractionating vats, where it has been purified and separated from the other rare-earths by fractional crystallization, was used. The absorption spectrum of a concentrated solution of the nitrates showed only the faintest traces of the neodymium and praseodymium bands. The contents of a large bottle containing five kilograms of the double nitrates was divided into four portions and placed in fourteen-inch (35 cm.) porcelain evaporating dishes. The dishes were filled with concentrated HCl and placed on steam-heated sand-baths. Each dish was suitably protected from drippings from the hood by wooden covers raised a few inches above the tops of the dishes and supported on silica bricks. Fresh acid was added daily as required and the evaporation continued for about three weeks, at the end of which time the nitrates had been completely converted to chlorides and all the ammonium salts had been expelled. The white solid was broken into lumps and heated on an

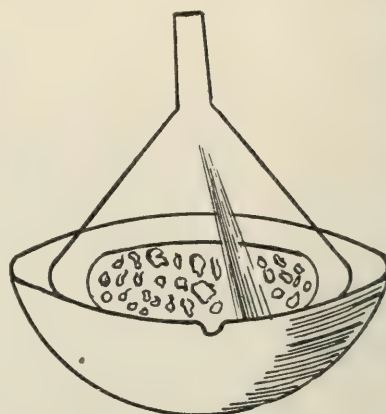


Fig. 1.

asbestos-covered hot plate to convert it to the monohydrated chloride. The final dehydration was carried out as follows (see Fig. 1): About 400–500 grams were placed in a ten-inch porcelain evaporating dish. A short-stem funnel about nine inches in diameter was inverted and placed over the salt. A layer of asbestos fiber was packed tightly around the outside edge of the funnel and plaster of Paris set over this. A glass tube passing through the stem of the funnel and reaching to just above the layer of chloride conducted in the dry HCl gas, which was passed at a rapid rate over the heated chloride. The salt was stirred around from time to time by means of a long, thick glass rod. The heating was done gradually and the progress of the dehydration could be watched, through the glass funnel, and its completion checked nicely. The anhydrous chloride was placed, while still warm, in dry glass vessels, and the corks paraffined in to exclude moisture from the extremely hygroscopic product.

The chloride prepared by this method melts to a clear, limpid liquid, and is suitable for electrolysis.

The process meets practically all the requirements—it gives a suitable product, it is rapid, inexpensive and simple, the progress and completion of the dehydration can be watched, overheating may be avoided, and large amounts of chloride prepared in the minimum amount of time. Chlorine and sulphur monochloride may be used in addition to the dry HCl gas, but this was not found necessary, as the water was driven off rapidly and completely without their presence.

It was observed that the anhydrous rare-earth chlorides may be partially converted into oxides or oxychlorides if they were carelessly heated in the presence of air. For this reason experiments were conducted on melting the chlorides in a non-oxidizing atmosphere in a Rose crucible. In the presence of carbon dioxide some oxychloride was formed, and in an atmosphere of carbon monoxide a crust of brownish oxide appeared.

The best method of melting the anhydrous chlorides without decomposition was found to be by heating a small portion in a covered crucible until a clear melt was obtained, and then introducing successive small portions of the chlorides to the melted portion. In this manner circulation of air is avoided, as the crucible is kept covered. A good way is to first melt sodium or potassium chlorides, or a mixture of these, and then to add small amounts of the rare-earth chlorides, keeping the crucible covered as much as possible. A small amount of oxide or oxychloride will "gum up" the entire melt, and for electrolysis this condition must be carefully guarded against.

Preparation of Anhydrous Fluorides.

Another salt required in large amounts was the anhydrous mixed fluorides, RF_3 . This preparation involves some of the difficulties encountered in the preparation of the anhydrous chlorides. The fluorides are more stable and less hygroscopic than the chlorides, but they are more corrosive in their action on apparatus. Porcelain vessels can not be used, and one is almost entirely limited to lead vessels in the preparation of these fluorides. However, lead linings are easily placed in evaporating dishes, especially in the large enameled iron ones, and five-gallon jars made of lead containing 10 per cent. antimony were found very convenient in this work.

A few methods are found in the literature for the preparation of anhydrous cerium fluoride, CeF_3 , but not many. The fluorides of cerium, especially the hydrated ones, are insoluble in water and are gelatinous precipitates usually obtained by double decomposition.

The tetrafluoride $CeF_4 \cdot H_2O$ is found in nature as fluocerite, and when this mineral is heated it decomposes, forming the impure anhydrous fluoride CeF_3 .⁴² By precipitating cerous nitrate with hydrofluoric acid Jolin⁴³ obtained a gelatinous precipitate, which after drying over sulphuric acid corresponded to the formula $2CeF_3 \cdot H_2O$. When this substance was heated it decomposed, leaving a residue of oxide.

In the preparation of the anhydrous rare-earth

fluorides both dry and wet methods were tried. Hydrofluoric acid gas was passed over a small amount of the pulverized carbides placed in an iron tube and heated to a temperature of about 200°. The hydrofluoric acid gas was prepared by heating CaF_2 with concentrated H_2SO_4 in a copper retort. Some fluoride was formed, but was contaminated with carbon and undecomposed carbide, and the method was regarded as unsuccessful.

The action of concentrated HF on the oxides was tried. A small amount of the mixed oxides was heated in a platinum dish with successive portions of concentrated HF. The action was vigorous at first, but soon stopped, and the residue was a mixture of oxide and fluoride.

As the anhydrous fluorides were required, a process in which no water was used obviated the subsequent removal of that water, and seemed to be at least worthy of trial. The chlorides were boiled with absolute alcohol until a concentration solution was obtained, which was transferred to a lead tub placed in hot brine, so that the precipitation might be done from a hot solution, and HF gas passed into the hot chlorides. The objections to this method are that the fluorides so prepared are contaminated with some chloride. Furthermore, the saturation of the hot alcohol with HF gas is a very slow process, and the fluorides are extremely difficult to filter on account of their gelatinous nature. If the precipitation is done in the cold, the fluorides come down in a slimy condition almost impossible to handle, hence the reason for precipitating from hot solution. While the precipitation may be done by the action of a concentrated solution of hydrofluoric acid on the aqueous solution of the chlorides, the fluorides settle far less readily in water than in alcohol. Consequently, on account of the above reasons, the next modification in the process was to dissolve the mixed oxides in concentrated HCl, concentrate the solution and add the requisite amount of concentrated HF to the hot solution. After allowing the precipitate to settle, the supernatant liquid was siphoned off, alcohol added, the whole stirred thoroughly, the precipitate allowed to settle, the liquid siphoned off and the treatment with successive portions of alcohol repeated several times. The fluorides were dried at a low temperature, and were pink in color. They melted at a fairly high temperature (about 900–1000°) to a clear liquid, and the process was satisfactory except for the time required for the precipitates to settle.

In order to flocculate the fluorides so that they could be more easily filtered, the precipitate of the fluorides was placed in a round-bottom Jena flask about half full of absolute alcohol, and heated in an autoclave at a temperature of 130° and a pressure of 90 pounds per square inch. The product so treated seemed to settle somewhat more rapidly, but filtered very slowly indeed.

After many trials, the most satisfactory preparation of the anhydrous fluorides was found to be best effected by the following method: About a kilogram of the

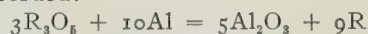
mixed oxides was placed in a large porcelain evaporating dish and digested in a steam closet with concentrated HCl until a clear concentrated solution of the chlorides was obtained. The hot solution, containing only a slight excess of hydrochloric acid, was transferred to a five-gallon lead jar and concentrated HF added to complete precipitation. The fluorides were allowed to settle somewhat, as much of liquid siphoned off as was possible, and washed twice with hot water and several times with 95 per cent. alcohol. Only a few minutes' time was allowed after each washing for the precipitate to settle. The fluorides were then placed in a lead-lined cage-centrifuge, and most of the remaining alcohol removed in this manner. Absolute alcohol was added and the solution evaporated to dryness without decanting. The absolute alcohol dehydrates the centrifuged fluorides very well. They were then dried at 100°, and the temperature raised to 200° at the end. About six kilograms of the fluorides were prepared in this manner. The process is a fairly satisfactory one, and as no filtering is done, the method is fairly rapid.

PREPARATION OF METALLIC CERIUM AND MISCHMETALL.

Thermal Reductions.

Thermal reductions were tried in the hope of producing rare-earth metals by this simple means. Previous work of this nature has already been referred to.¹⁵⁻¹⁹ Magnesium and calcium shavings and aluminum powder were used as reducing agents on the mixed oxides. These experiments were conducted in electrically-baked magnesia linings placed in graphite containers. Carbon and silicon were also used to reduce the oxides, but external heat was applied to give the high temperature required. No metal was formed in these last instances but the carbides and silicides respectively. The carbide RC_2 is pyrophoric, but the silicide RSi_2 is not. Reductions using magnesium and calcium in excess gave alloys, many of which were pyrophoric.

Several trials to reduce the oxides with aluminum are here recorded:



150 grams mixed oxides require 27 grams aluminum.



507 grams barium peroxide require 54 grams aluminum.

The following charge was weighed out, intimately mixed and fired by means of magnesium wire and thermit igniter.

	Grams.
Mixed oxides.....	150
Aluminum powder.....	40
Barium peroxide.....	120

The reaction was vigorous, but not violent. A five-gram lump of metal and many small globules were obtained. The specific gravity of the metal was greater than that of aluminum.

In another experiment the following charge was used:

	Grams.
Mixed oxides.....	200
Aluminum powder.....	61
Barium peroxide.....	200
Black thermit mixture.....	50

The black thermit was used to produce a higher temperature and also for the reason that the affinity of cerium for iron was thought to be greater than that of cerium for aluminum; 35 grams of hard-brittle alloy were obtained, but the content of rare-earth metals was low.

In the case of these thermal reductions, either an alloy, a compound or a lower oxide of the rare-earths was obtained. Owing to the high heat of formation of these oxides, the failure of alumino-thermics in the production of metal was only to be expected. The writer believes that a study of the equilibrium conditions of these reactions would form an interesting and valuable research and might result in the discovery of lower rare-earth oxides.

Earlier Work on the Electrolysis of the Anhydrous Chlorides.

The previous work on the electrolytic preparation of cerium has already been referred to. The method of Bunsen, which the earlier investigators used, is described as follows:⁴⁴ "In a porcelain crucible, in which the mixed chlorides of sodium and potassium has been melted, small amounts of anhydrous cerium chloride were introduced by means of a small porcelain spatula. An annular piece of iron was used as anode, and the cathode consisted of a platinum wire, protected by a short piece of clay pipe stem. The temperature of the fused bath was lowered until a thin crust formed on the surface of the bath, when the electrolysis was commenced. Globules of cerium rose to the surface and burned with explosive force. Hillebrand and Norton thus obtained metallic globules to the amount of six grams."

At one time the writer tried to duplicate the above experiment, but was unable to collect any metal. The platinum cathode was badly attacked; in fact, part of it melted off, due to formation of an alloy with cerium.

For a survey of Muthmann's work on the rare-earth metals the reader is referred to the original reference.²³⁻²⁴ The type of vessel used in the electrolysis of the chloride is shown in Fig. 2, and is now generally known as the Muthmann cell. It is a semi-water-jacketed vessel, constructed of copper, and may be used with or without the heating circuit. The principal objection which the writer has to the cell is its complicated nature. The cathode should be insulated carefully, and this is difficult, as the asbestos packing is attacked by cerium metal, and during the course of the electrolysis the insulation is apt to be destroyed and the walls of the vessel may act as cathode, with the subsequent contamination of cerium with copper. This is especially liable to occur if the temperature of the bath is too high. The heating circuit must also be insulated from the walls, and the carbon heating rods are liable to crack and break. Unless the contents of the cell are poured or tapped at the completion of the electrolysis, the entire cell has to be dismantled after each run. When worked on a small scale, the manipulation of this electrolytic cell is a troublesome and difficult operation.

In the present research, numerous runs were made before more than traces of metal were obtained. It is believed by the writer that an account of failures is often fully as important as that of successes, as it is only by correction of faults that successful results are obtained. Therefore a brief account of the earlier unsuccessful attempts to produce rare-earth metal are here given. It was only by a complete understanding of the reasons for failure that a successful solution of the problem was accomplished.

The different types of cells used where anhydrous mixed chlorides were employed as the electrolyte are shown in Figs. 3 to 5.* They were all constructed

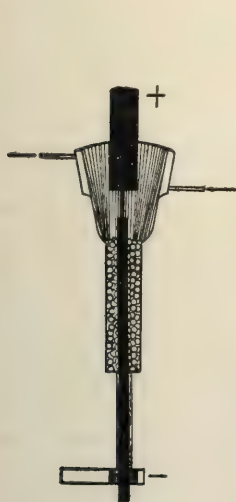


Fig. 2.

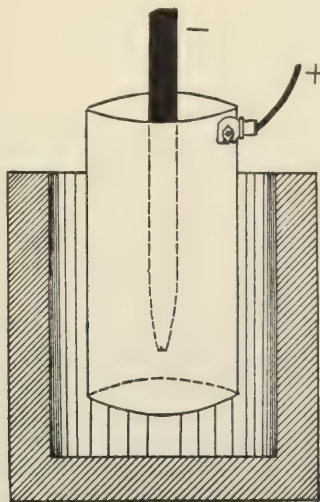


Fig. 3.

of the same material, graphite. The anodes were of graphite, but in the case of the insulated cathodes these were sometimes of graphite and sometimes of iron. In many cases where a graphite crucible was used as both containing vessel and cathode, the melting was done in a resistor furnace, and then the electrolysis was begun. In some instances the heating was done by alternating current, and could be maintained and regulated during the course of the electrolysis. The melting of the electrolyte was sometimes done by a small thin carbon heating rod placed between electrodes, as shown in Fig. 2. An arc could not be used to melt the chlorides, as they are decomposed at that temperature.

The principal difficulties encountered in these experiments were the following:

1. The salt would not melt to a clear liquid.
2. The electrolyte would remain liquid for a time, but would eventually solidify.
3. The IR drop across the cell and the amperage would vary.
4. The anode would not functionate properly.
5. On completion of the electrolysis, no regulus of metal was obtained.
6. Minor difficulties, such as short-circuiting of insulated cathodes, leakages, fracture of electrodes,

* The crucible shown in Fig. 4 was split longitudinally into two sections, which were cemented together by graphite-molasses paste and clamped firmly together. This makes a very convenient form of electrolytic cell, as it can be easily dismantled, and also very quickly reassembled.

etc., liable to happen in any fused electrolysis, were encountered.

The reasons for the above difficulties were found by experience to be explained as follows:

1. If the chlorides did not melt to a clear liquid, then either the chlorides were not anhydrous or they were decomposed in the process of fusion. The proper manner of melting the chlorides has already been discussed in sufficient detail.

2. The "gumming-up" was caused either by the formation of a higher melting salt, as the oxide or carbide, or the temperature of the bath was too low (see 4, below).

3. As the generator voltage and the external resistance were constant, changes in the voltage across the cell and the amperage were caused by a variation of the internal resistance of the cell. This variation was caused by the following factors: Change in temperature of the bath; depletion in the electrolyte, or segregation, such as double layers, etc.; formation of intermediate products of varying resistance, such as sub-chlorides; differences in thermal conductivity of the electrolyte at different stages of the electrolysis; etc. It was found that the potential difference and the amperage of any one cell can vary only between certain limits for successful electrolysis. The heating value of the current (C_2R) in cases where no external heat is applied must be such as to keep the temperature of the bath at a certain value. If the temperature of the electrolyte is too high it is impossible to successfully electrolyze in the case of cerium chloride.

4. The function of the anode was (1) to cause the separation of chlorine and (2) to supply most of the heat necessary to keep the bath fused.

(1) In all these experiments the amperage was such that, if the cell was working properly, there was a copious evolution of chlorine gas. In many cases the voltage across the bath and the amperage would be approximately the proper values, and yet very little chlorine would be evolved. This may occur under several very different conditions. If

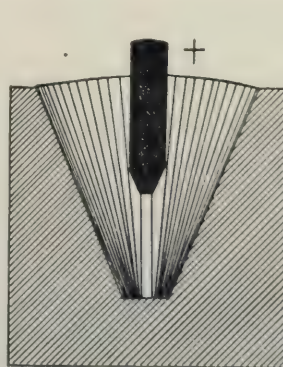


Fig. 4.

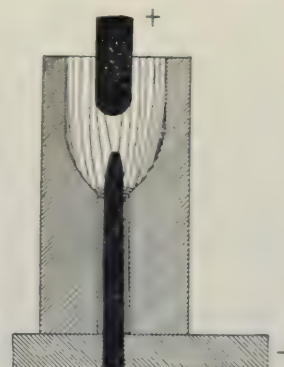


Fig. 5.

the temperature of the bath is low, the semi-fused chloride is a very good conductor, and the entire bath may behave as a conductor of the first class. In this case practically no chlorine will be evolved. Again, if the temperature of the bath is too high, little chlorine is given off. This is due to the fact

that at the cathode the chloride is partially reduced to subchloride, which diffuses to the anode and is there oxidized by the chlorine to chloride. There is a narrow limit of temperature where true electrolysis occurs, that is, where anhydrous CeCl_3 is decomposed by the current to metal and chlorine.

(2) In cases where the containing vessel acted as the cathode, anodic current density was much greater than the cathodic, consequently most of the heat was supplied to the cell by the anode. In the preliminary experiments the anodes were of graphite, but with the same diameter anode and the same current the heating is greater with a carbon than with a graphite anode. In some of the later runs carbon was used as the anode material for the reasons mentioned above. If the diameter of the anode is too great, a large current is required to keep the bath molten. Besides, the anode is brought nearer the walls and most of the current may pass through the upper part of the cell. This should be avoided, as the path of least resistance for the current should be from the anode to the bottom of the cell, as this insures good circulation of the electrolyte and the deposition of the metal in a united form. If metal is deposited on the upper walls, some is apt to become oxidized by contact with the air, and this may result in the bath becoming viscous.

5. Many of the reasons for failure to obtain a regulus of metal have been given above. The metal may be deposited in a finely-divided, unfused condition, and may be disseminated throughout the body of the electrolyte. It may be totally or partially soluble in the electrolyte (for instance, Li in LiCl), or the metal may react with the products at the anode (as chlorine) or the material of the cell (with copper forming an alloy, or with graphite forming a carbide).

Electrolysis of the Anhydrous Fluorides.

When it was found that the electrolysis of the chlorides was such a difficult process, it was thought that the electrolysis of some other salt might be more easily effected. Muthmann^{24(c)} has used the solution of the oxides in the fused fluorides, similar to the process for the production of aluminum.

The anhydrous mixed fluorides melt at a temperature of a little over 900° , and dissolve the mixed oxides with avidity. The electrical conductivity of the molten fluorides is low, but increases rapidly with addition of oxides. The solution containing about 20 per cent. of oxides conducts very well.

The first cell tried with the fluorides contained a graphite cathode insulated from the graphite vessel by a porcelain ring. During the electrolysis the porcelain was badly attacked by the fused fluorides. Even a Dixon crucible was badly eroded, as the fluorides attacked the silicate binder. It was found that graphite was one of the few substances that would withstand the high temperature and the action of the fused fluorides. A vessel made of graphite plates, luted on the edge with graphite-molasses paste, clamped together with iron bands and previously baked, leaked during the electrolysis. Al-

though the vessel was embedded in magnesia flour to prevent oxidation, the high temperature of the bath (well over 1000°) caused the luting to break down.

A summary of the results of the runs using fluoride-oxide electrolyte are here given.

1. 2,500 grams anhydrous mixed fluorides were melted in a resistor furnace. The fused fluorides readily dissolved 450 grams of mixed oxides. The molten bath was electrolyzed, using 450 amperes at a pressure of 14 volts. 10-15 grams of impure metal were obtained. The electrolysis was unsatisfactory, as the anode was not properly "wet" by the electrolyte. The active surface of the anode should have been much greater. A layer of carbide was found on the bottom and sides of the crucible.

2. A graphite box, inside dimensions $4\frac{1}{2} \times 5 \times 6$ inches ($11 \times 12 \times 15$ cm.), which was chiseled from a solid graphite block, was used as the electrolytic vessel. The anode was made as follows: A graphite block about 16 in. (40 cm.) long, 3 in. (8 cm.) wide and 2 in. (5 cm.) thick was cut at one end so as to present three blades, each $\frac{1}{2}$ in. (1 cm.) thick and 3 in. (8 cm.) wide. This increased the active surface of the anode and resulted in its functioning properly. The fluorides were melted by a carbon heater placed between the electrodes. As soon as a small amount of the fluorides was melted, the heater was removed, the anode lowered and alternating current turned on. 1,000 amperes at 24 volts for about 25 minutes were required to melt 4,300 grams mixed fluorides. Mixed oxides were added gradually and then direct current switched on. 650-750 amperes at a pressure of 10 volts were used. Oxide was added gradually during the course of the run, which was continued for about an hour, at the end of which time the solution solidified. 4,300 grams fluoride and 1,600 grams oxide were used in all. Small amounts of metal were scattered throughout the mass, but no regulus was obtained. At the bottom of the vessel was found a black layer of carbide. The melting point of the fluoride-oxide mixture was about 1400° .

The principal difficulties encountered in the electrolysis of the oxides dissolved in the fused fluorides were:

1. Oxides must be added to the fluoride to make a sufficiently conductive solution, and the melting-point of the bath is very high.

2. At the high temperature of the bath, rare-earth metal and graphite combine to form carbide.

Attempts were made to electrolyze a solution of the oxides dissolved in a mixture of fused potassium fluoride and rare-earth fluorides. Violent explosions ejected a large portion of the electrolyte during the run, due perhaps to the deposition of alkali metal, which was immediately vaporized at the temperature of the bath.

One of the principal difficulties in all the previous electrolyses had been the formation of carbides, which made the bath viscous and unfit for electrolysis. It was thought that if a non-carbon cell was used, the formation of carbide would be less likely to occur,

as the only carbon in the cell would be the anode. On account of their corrosive action and high melting point the fluorides could not well be used in other than carbon vessels. It was therefore decided to try the electrolysis of the mixed chlorides in a wrought-iron vessel.*

Later Work on the Electrolysis of the Anhydrous Chlorides.

1. The electrolytic vessel was a thin-walled wrought-iron crucible about 3 in. (8 cm.) high and 2 in. (5 cm.) average diameter. The anhydrous mixed chlorides were fused by means of a thin carbon rod, heated electrically to incandescence, and electrolyzed with a current of about 50 amperes for several hours. The electrolyte remained fluid during the entire course of the electrolysis. About 30 grams of semi-fused metal were obtained.

The iron crucible was not attacked. The success of this run led to experiments on the best conditions for electrolysis on a larger scale.

2. The electrolytic vessel was a large iron crucible $5\frac{1}{2}$ in. (14 cm.) maximum inside diameter and 7 in. (18 cm.) high. The anode was a carbon rod $1\frac{1}{2}$ in. (4 cm.) in diameter. A small amount of sodium chloride was fused, and the mixed chlorides were added in small amounts until a fused bath was obtained. The electrolysis was maintained with a current of 130 amperes for four hours at a pressure of 12-18 volts. Small amounts of anhydrous potassium fluoride (about 10 grams at a time) were added occasionally to dissolve what little oxide was formed and so keep the bath perfectly fluid. The amount of additional salts used (KF plus NaCl) in all was about 10 per cent. by weight of the rare-earth chlorides. A lump of partially fused metal was obtained, which when re-melted under NaCl weighed 120 grams. The number of ampere hours used was 520, and the ampere efficiency was $13\frac{1}{2}$ per cent. The crucible was not attacked.

3. The object of this run was to try the value of an insulated cathode. Previous experience had taught that if the insulated cathode was iron and a fairly large current used (about 200 amperes) the iron cathode would become so hot that an alloy would be produced. Consequently iron was not used as the cathode in this electrolysis. The electrolytic vessel consisted of a 6-in. (15 cm.) length of a 3-in. (8 cm.) iron pipe screwed into a reducing-cap carrying a short piece of 2-in. (5 cm.) pipe. The cathode consisted of a long rod $1\frac{1}{2}$ -in. (4 cm.) graphite insulated from the sides of the 2-in. (5 cm.) pipe by asbestos fiber and encased at the bottom in plaster of Paris. A sketch of this cell is shown in Fig. 6. The anode was a graphite rod $1\frac{1}{2}$ in. (4 cm.) in diameter. A current varying from 180 to 200 amperes at a pressure of 20 volts was used for nearly four hours. A regulus of metal weighing 135 grams was found at the bottom of the vessel. Below the metal was a black layer of carbide. The number of ampere hours was 712, and the ampere efficiency was 11 per cent. The electrolyte consisted of the mixed chlorides, to which

were added, during the course of the run, small amounts of anhydrous potassium fluoride, sodium chloride and barium chloride. The object of the last-named salt was to increase the resistance of the bath so that the electrolyte was kept well fused and metallic conduction of the bath prevented. It must be remembered that where a graphite anode was used, a higher voltage was required to keep the bath fused.

The results of the above three experiments showed: (1) That rare-earth metal could be produced by electrolysis of the chlorides in iron vessels; (2) that the use of an insulated cathode of graphite gave a lower current efficiency and resulted in some of the metal being converted to carbide; (3) that it was necessary to regulate the temperature of the bath so as to have the electrolyte well fused and yet well below the alloying temperature of iron and rare-earth metal; and (4) that control of the electrolysis could be maintained by judicious addition of small amounts of potassium fluoride, sodium chloride and barium chloride.

The above experiments in which the anhydrous mixed chlorides were used were so successful that the method of electrolysis was applied to pure anhydrous cerous chloride, and the runs are here described.

1. The electrolytic vessel was a thin-walled wrought-iron crucible, maximum diameter about 4 inches. The anode was a round graphite electrode 1 inch in diameter, and the iron crucible was made the cathode. A small amount of sodium-potassium chloride was first melted, and then cerous chloride added. During the course of the electrolysis, rather large amounts of the alkali chlorides were used. A current of 110 amperes was employed for two hours, at the end of which time the electrolyte solidified. Forty grams of fairly well-fused metal was obtained. The number of ampere hours was 220, and the ampere efficiency was 11 per cent. Too much alkali chlorides was added during the electrolysis, and this fact, together with the high temperature of the bath,* accounts for the efficiency.

2. A crucible similar to the one described in the above experiment was used both as the containing vessel and cathode. A corrugated graphite anode $\frac{5}{8}$ in. (1.6 cm.) in diameter was used. 250-300 grams of anhydrous cerium chloride and about 10 per cent. sodium chloride were used. The electrolysis

* In many electrolyses a high ampere efficiency is obtained only if the bath is kept near its melting point. As the temperature is raised the efficiency decreases. This is especially true in the case of fused lead chloride and fused caustic soda, where if the temperature of the bath is high, no metal at all is obtained. See these Transactions, 19, 167-168 (1911) (Discussion).

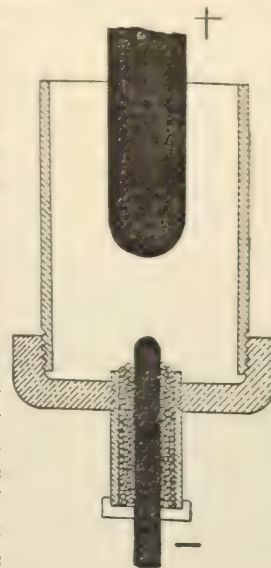


Fig. 6.

* Kindly suggested by Dr. W. H. Walker, of the Mass. Inst. Tech.

was continued for $1\frac{1}{2}$ hours, using 75 amperes at 15 volts. The bath was kept near its melting-point, so that there was no danger of a cerium-iron alloy forming. 65 grams of cerium metal were obtained. The number of ampere-hours was 112, and the ampere efficiency was 33 per cent.

3. It was decided to try the electrolysis on a larger scale. When the mixed rare-earth chlorides were electrolyzed in a large iron crucible, it was difficult to remove the solidified salt after the run was completed. The chlorides, after cooling, form a hard, vitreous mass, upon which even a cold-chisel has little effect. The removal of slag and metal was always accomplished with difficulty and loss of some material. To obviate this difficulty a 7-in. (18 cm.) length of a 3-in. (8 cm.) iron pipe, screwed into a cap for a bottom, was used as the electrolyzing vessel (see Fig. 7). Sodium chloride was melted first, and cerous chloride added until the fused mixture conducted well, when the carbon electrode, $1\frac{1}{4}$ in. (3 cm.) in diameter, was lowered until it was within an inch or so of the bottom; the voltage then sank to the proper value, 12 volts, and electrolysis began. The volume of

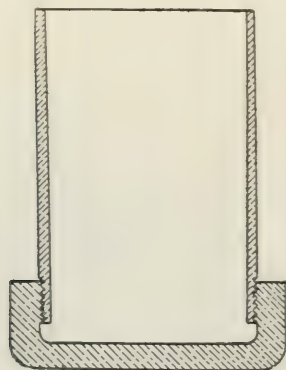


Fig. 7.

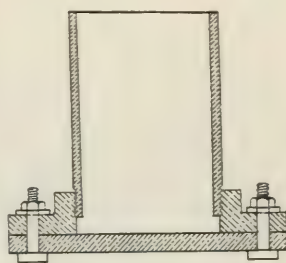


Fig. 8.

the bath, of course, constantly decreases during the electrolysis, and fresh cerous chloride must be added from time to time. About every forty minutes the anode was raised until it just dipped below the surface of the bath. This increased the voltage across the bath and caused a rapid heating of the electrolyte. After a few minutes the anode was lowered until the voltage was properly adjusted, when electrolysis recommenced. The voltage varied from 12 to 14 volts, and the average current used was 200 amperes, for four hours. The electrolyte became slightly viscous toward the end of the run, but the electrolysis proceeded satisfactorily, as was indicated by the appearance of the bath, the voltage across the cell and the evolution of chlorine. Over a kilogram of cerous chloride was used. A well fused ingot of metal weighing 580 grams was obtained. The number of ampere hours was 800, and the ampere efficiency was $41\frac{1}{2}$ per cent. The cap could not be removed at the completion of the electrolysis, but the crucible was unattacked by the cerium. The small amount of iron introduced was caused by oxidation of the heated vessel near the top, the solution of this iron oxide in the electrolyte and its immediate reduction to metal when in contact with cerium.

4. In order to facilitate the removal of electrolyte and metal at the end of a run, the following vessel was devised: It consisted of a 3-in. (8 cm.) iron pipe screwed tightly into a 5-in. (13 cm.) iron flange, to which a bottom plate was attached by means of four large bolts and nuts (see Fig. 8). The electrolyte was cerous chloride containing a small percentage of sodium chloride, to which very small amounts of potassium fluoride and potassium fluoride-barium chloride mixture were added when required (about every half hour or so). The function of these additional salts has already been explained in detail. The voltage was kept at its proper value, which should not be greater than 15 volts. The average current used was 200 amperes, for three hours. The electrolysis required attention about every twenty minutes; that is, the anode needed slight adjusting or the temperature had to be corrected. An ingot weighing 380 grams was obtained. The number of ampere hours was 600, and the ampere efficiency 36.5 per cent.

The electrolyte remained liquid during the entire course of the electrolysis. About $1\frac{1}{2}$ kilograms of cerous chloride were used. The cell held perfectly, and at the end of the run the electrolyte and metal were easily removed. This type of electrolytic vessel is highly recommended for similar work. Care should be taken that the flange and bottom plate are well faced and that the lap is wide enough (at least $1\frac{1}{2}$ in. (4 cm.)).

ANALYSIS OF CERIUM AND "MISCHMETALL."

Two methods of analysis were used in this research for the determination of cerium:

1. *Gravimetric.*—The cerium group was separated from all the other metals by precipitation of the oxalates in faintly acid chloride or nitrate solution, by means of boiling oxalic acid. Calcination of the oxalates at blast lamp temperature gave the oxides (in the case of cerium the dioxide CeO_2) which were weighed.

2. *Volumetric.*—A modification of Browning's⁴⁵ method was used. It depends upon the oxidation of cerous salt to ceric, in alkaline solution, by means of potassium ferricyanide. Browning determined the excess of ferricyanide.

The modification was as follows: A slight excess of a dilute solution of potassium ferricyanide was added to the solution of cerous salt, and KOH added. This precipitation was usually done in a bottle, which was afterwards centrifuged. The supernatant liquid was decanted through a small Gooch filter to guard against any loss of precipitate. The ceric hydroxide was washed two or three times with hot concentrated KOH to remove the ferro- and ferricyanides centrifuging after each washing. The ceric hydroxide was then treated with potassium iodide solution, whereby the cerium is reduced to the cerous state and free iodine liberated, which latter is determined by titration with thiosulphate. By this method cerium may be determined in the presence of thorium and the other members of the cerium group. This method is accurate to one-half per cent.

Grams cerium present.	Grams cerium found.	Error, gram.	Error, per cent.
0.22648.....	0.22697	0.00049	+0.2
0.22648.....	0.22657	0.00009	+0.04
0.22648.....	0.22697	0.00049	+0.2
0.22648.....	0.22752	0.00214	+0.5
0.22648 Ce.....	0.22737	0.00089	+0.4
0.4 Th(NO ₃) ₄			
0.11328 Ce.....	0.11388	0.00060	+0.5
0.10 La ₂ (SO ₄) ₃			

Analysis of a sample of "mischmetall" by the volumetric method showed a cerium content of 70.5 per cent.

Analysis of metallic cerium prepared in Run 1, above, showed the following composition:

Per cent. cerium.	Per cent. iron.
97.5	1.2
97.8	
97.8	

The determination of cerium by the gravimetric method in the cerium metal prepared in Run 4, above, showed 97.8 per cent. cerium.

Analysis of cerium cast into rods in an iron mold was as follows:

	Per cent.
Cerium.....	93.6
Iron.....	4.5
Insol. residue (oxide).....	0.53
Magnesia (from MgO lining).....	0.4
Carbon.....	0.88
Chlorine.....	0.07
	99.98

PURIFICATION OF METALLIC CERIUM.

The chief impurities of cerium (amounting in the aggregate to about two per cent.) obtained by the method previously described consisted of iron, cerium oxide and cerium carbide, of which over one per cent. was iron.

Owing to the fact that metallic cerium is but slowly attacked by concentrated sulphuric acid, filings of the metal were boiled with this acid. All of the iron was not dissolved, and the method is worthless for purification purposes.

The magnesium alloys of cerium, containing from 50 to 85 per cent. cerium, are brittle and may easily be pulverized to a fine powder. When digested with strong sulphuric acid for a few hours, the residue contains cerium, magnesium and iron. This method is also worthless.

The best method of purification consists in preparing the cerium amalgams. The amalgams are prepared by boiling mercury with cerium in a long iron pipe arranged with a condensing tube at the top. Solid amalgams are easily obtained by this method. The iron and impurities float to the top and may be skimmed off. The amalgams carefully prepared give only a very slight test for iron. The cerium and mercury may be separated by distilling the latter, but this must be done in a high vacuum to prevent oxidation of the cerium. A high temperature is required to drive off all the

mercury. The amalgam should be placed in a magnesia vessel, and this in turn heated in an evacuated quartz vessel. The high temperature required would cause the collapse of an evacuated glass vessel.

PHYSICAL PROPERTIES OF METALLIC CERIUM.

In the determinations of the physical properties, metal of approximately 98 per cent. of cerium was used, unless otherwise specified.

1. *Atomic Weight*.—The atomic weight of cerium, determined from pure salts, is 140.25.

2. *Specific Gravity*.—The specific gravity determinations were made in a 50 cc. pycnometer of cylindrical form, with thermometer ground in central neck and with fused-in capillary tube at side. The liquids used were pure benzene and toluene, which have no chemical action on cerium. Several different specimens of metal were used for these determinations. The weight of metal taken varied from 3.4 to 11.2 grams. The average of determinations gave 6.92, at 25° C.

3. *Molecular State of Aggregation*.—No reference was found in the literature as to the crystallographic properties of cerium. Attempts were made by the writer to obtain crystals, but without success. The interior of many ingots of cerium were highly crystalline, especially in the center of blow-holes. The best condition for crystal growth is slow cooling from the molten condition. In order to aid the formation of crystals, a small quantity of cerium was melted under lithium chloride. The crucible was kept just hot enough to prevent the lithium chloride from solidifying, and was maintained at this temperature for several hours. The melting point of lithium chloride (about 550°) is somewhat below the melting point of cerium, and under these conditions the formation and growth of crystals would be expected. However, no definite crystals of cerium were obtained.

In order to examine the inner structure of cerium, photomicrographs of different specimens were made. The specimens were prepared by dry-polishing, and were etched with alcoholic HCl. An examination

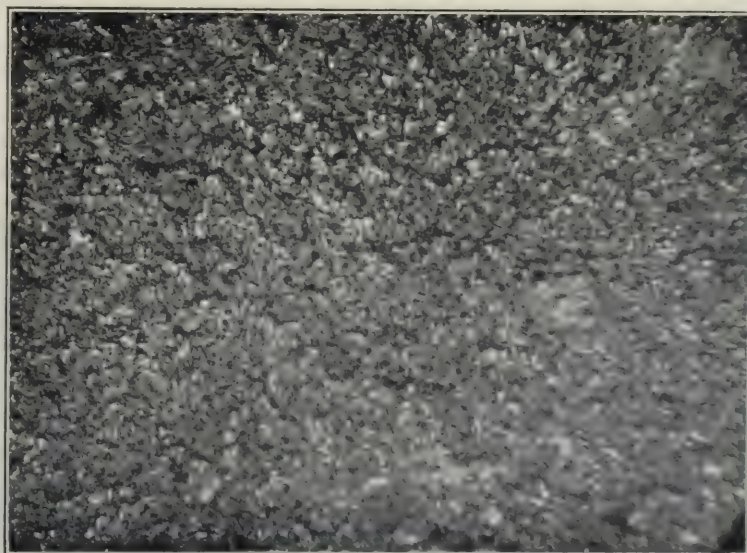


Fig. 9.

of these photomicrographs (see Fig. 9) shows homogeneity of structure.

4. *Hardness*.—For the determination of hardness the scleroscope was used. The hardness of cerium varies, depending upon whether the surface of the metal is rolled, freshly cut, or old. The average value of the hardness for rolled surface was 25.9. The average for freshly cut surface was 9.5. (The reading 100 is the hardness of the standard steel test plate.)

5. *Tenacity*.—Cerium is malleable and highly ductile. A strip of cerium was rolled to a thin sheet of a thickness of 0.015 mm. Cerium metal can easily be cut with a knife or scissors, and can be machined fairly well, although there is some tendency for the metal to buckle, as does lead.

6. *Electrical Conductivity*.—In order to make these measurements, a test bar was necessary. A good method of obtaining a known length and cross-section of metal is to take a short piece of capillary tubing, apply suction at one end, insert the other in the molten metal and so fill the tube. On account of the corrosive action of cerium on glass and silica, it was impossible to use this method.

It was difficult to cast cerium into solid rods, owing to its rapid oxidation in air. The following mold was prepared, which was so designed that molten cerium could quickly be poured into it from the melting crucible and oxidation prevented: A wrought-iron pipe, $\frac{1}{4}$ in. (0.65 cm.) inside diameter and about 5 in. (13 cm.) long, was screwed into the iron base. A piece of cast iron was turned on the lathe to the shape of a small funnel, and was screwed into the wrought-iron pipe. The cerium was melted in a magnesia-lined graphite crucible under a covering of fused salt. The mold was heated to a dull redness, and the entire contents of the crucible poured suddenly into the mold. Very little oxidation or burning of the metal occurred. A rod of cerium 3 in. (7.5 cm.) long was obtained. This metal contained 93.6 per cent. cerium and 4.5 per cent. iron. Although the inside of the pipe had been carefully cleaned, it was impossible to prevent contamination of the cast cerium with iron. As it was necessary to pre-heat the mold, a small amount of iron oxide necessarily formed, and, on contact with cerium, was reduced to metal and entered the rod as an impurity. The rod was turned down to size on the grinder.

The electrical conductivity measurements were made by the voltmeter-ammeter method. The potential drop was taken over one inch of test bar, and all measurements were made at room temperature. The current was varied from 6 to 18 amperes. The specific resistance of the sample was found to be 71.6 microhms per centimeter cube.

7. *Magnetic Properties*.—Stefan Meyer⁴⁶ has measured the magnetic susceptibility of many metals, among them that of cerium. He gives the atomic magnetic susceptibility of cerium ($K \times 10^{-6}$) equal to 34. He does not state the purity of the cerium

used. The writer made no attempt to measure the magnetic susceptibility of cerium, but simply to determine if cerium is dia- or para-magnetic.

A small piece of cerium was suspended by a silk thread in a magnetic field of intensity about 5,000 lines per cubic centimeter. The metal so tested was paramagnetic, but not strongly so.

Cerium amalgam practically free from iron was sealed in a small glass tube and tested in a magnetic field. It was weakly but definitely paramagnetic. From these determinations it was concluded that pure cerium is paramagnetic.

8. *Melting Point*.—It was impossible to use the ordinary thermocouple method to determine the melting point, as no suitable protecting mantle could be found. Silica and porcelain are both attacked by cerium at its melting point. Magnesia, which is unattacked, is too porous a material for this purpose.

An attempt was made to obtain a cooling curve of cerium. About 60 grams of the metal were melted in a magnesia crucible in an electric resistor furnace and readings were taken with a small copper-constantan couple placed in a porcelain mantle. It was thought that although the porcelain would be attacked somewhat, an approximate value for the melting point might be obtained. However, the cooling curve showed no constant temperature period and was worthless.

A small piece of cerium was attached to two long copper wires by means of small copper bolts and nuts, such as are used by watchmakers. Good electrical connection was obtained in this manner. The cerium was placed in a long Jena glass tube, sealed at one end and closed at the other by means of a rubber stopper, and so arranged that the tube could be evacuated. This was then placed in a tube furnace containing a calibrated thermocouple. A small amount of current was passed through the cerium, and when connection was severed, an electrical gong sounded. This scheme of obtaining the melting point did not work as the rubber stopper connection did not give a perfectly air-tight joint. The small amount of air in the tube combined with the cerium as the temperature increased. This caused a higher vacuum to be produced, with the result that more air entered the tube, and, upon subsequent repetition of this process, all the cerium was oxidized before the melting point was reached.

The approximate melting point was determined by heating a small quantity of cerium in a magnesia-lined graphite crucible and reading the temperature at which the metal softened by means of a thermocouple placed just above the metal. This crude method gave the approximate melting point as about 700°.

The real melting point of cerium was determined as follows: A small piece of cerium foil was fastened to two bent platinum wires by means of small copper bolts and nuts, and placed in a small glass bulb and the platinum wires sealed through the glass. The bulb was then evacuated by means of a mercury rotary pump, and sealed. A small incandescent lamp was

connected in series with the cerium, which was heated in an electric muffle furnace. The temperature was read by a calibrated thermocouple. The melting point of the cerium was very definite, and occurred at a temperature of 635°C . The tube collapsed somewhat, but the method gave satisfactory results.

9. *Ultimate Strength*.—The same test bar was used for these determinations as in the electrical conductivity measurements. The ultimate strength was determined in an Olsen testing machine. The average diameter of the test bars was 0.212 in. (0.55 cm.). There was no elongation with constant load at 350 pounds (159 kg.). The test bar broke with a snap (like cast iron) at 495 pounds (225 kg.). The ultimate strength is equal to 12,900 pounds per square in. (9 kg. per sq. mm.).

10. *Specific Heat*.—The specific heat was determined in a Joly differential steam calorimeter. The principal difficulty encountered was to get a suitable method of protecting the cerium from attack by the steam. The cerium was sealed in a glass tube, but this method was unsatisfactory, owing to the time necessary for exchange of heat due to the small conductivity of the glass. Another method employed for protecting the cerium was to coat it with a mixture of amyl acetate in collodion. However, this coating was attacked by the steam and was liable to peel. The metal was also placed in a small nickel box, but was attacked by the steam. The best method of protecting cerium, at the same time allowing for rapid heat interchange, was to wrap the cerium tightly in several thicknesses of tinfoil. Blanks were run on copper and tin foil to check the accuracy of this calorimetric method. The value for the specific heat of copper obtained with this steam calorimeter was equal to 0.0925. The specific heat of cerium (20 – 100°) was measured and found equal to 0.0524. Mendeléeff⁴⁷ gives the specific heat of cerium equal to 0.05.

11. *Heat Conductivity*.—No measurements were made on the heat conductivity, and no references were found in the literature relative to this property. The heat conductivity seems to be fairly high, and, if so, cerium is probably one of the exceptional metals which has a low electrical conductivity and high thermal conductivity.

12. *Latent Heat of Fusion*.—From observations on melting cerium, the latent heat of fusion seems to be fairly high. It has not been determined to my knowledge.

13. *Heat of Oxidation*.—The heat of oxidation was determined in a Mahler bomb calorimeter. Cerium must not be burned in contact with platinum, as it will alloy with the latter. The cerium filings were placed in a small magnesia crucible in the calorimeter. From one to two grams of cerium filings were used for each determination, under an oxygen pressure of about fourteen atmospheres. The average value of the heat of oxidation was 1,740 calories per gram, or 60,900 calories per gram equivalent ($\text{CeO}_2 = 243,600$). These values are probably correct within 4 or 5 per cent. It is difficult to obtain an accurate

value for the heat of oxidation where the products of combustion are non-volatile. The determinations in the case of cerium were unusually difficult to make, for the following reasons: The metal should be in a finely-divided form, but preferably in the shape of filings. When cerium is filed, care must be taken to prevent oxidation, owing to the low kindling point. A small amount of oxide forms in any case, and therefore makes the sample of metal taken non-uniform. If the filings are too coarse, oxide will fuse on the surface, and the metal in the interior will be unoxidized. Many of the difficulties encountered in the determination of the heat of oxidation of silicon⁴⁸ were met with here.

14. *Single Potential*.—Attempts were made to measure the single potential of cerium in the alcoholic solution of cerium chloride. No reliable measurement could be obtained, owing to the rapid formation of a film on the polished surface of the metal as soon as current flowed. The potential rapidly decreased as soon as the film appeared, which is almost instantaneous with the passage of current.

Measurements on the decomposition potential of the anhydrous mixed chlorides in absolute alcohol were made, using platinum electrodes. Gas was evolved at an applied electromotive force of 3.5 volts.

As the single potential of cerium could not be measured successfully, its value was calculated from the thermal data taken from Matignon's article on the anhydrous mixed chlorides:

Heat of formation of CeCl_3 (per 3Cl) = 270 calories

Heat of solution of CeCl_3 = 33 calories

The calculated decomposition potential of normal cerium chloride in aqueous solution is equal to 4.3 volts. Therefore the single potential of cerium in normal solution of its chloride measured against the normal calomel electrode is equal to -3.16 volts.

15. *Thermo-electromotive Force*.—Two small glass cells, protected by asbestos and fitted with wooden covers, were used. Standard thermometers with small stirrers attached were inserted through the cover. Cottonseed oil was used for the bath, and one of the cells was heated internally by means of several coils of resistance wire. The electromotive force was determined by the potentiometer method with a special piece of apparatus specially prepared for this kind of work. The thermo-electromotive force of cerium against copper is given in the table below and in the curve shown in Fig. 10. The current flowed at the hot junction from copper to cerium. The measurements are given in the following table:

Hot junction. Degrees C.	Cold junction Degrees C.	Electromotive force. Volt.
49.2	29.2	0.000075
100.0	25.0	0.000770
100.0	Red. to 30.0	0.000250
151.0	26.9	0.000399
151.0	Red. to 30.0	0.000387
200.5	29.7	0.000504
200.5	Red. to 30.0	0.000502

16. *Optical Properties*.—Cerium alone could not be used, owing to the fact that a thin film of oxide forms on the polished surface. Different alloys

of cerium were tried, and the best ones for this purpose were found to be the magnesium-cerium alloys. The preparation of samples had to be done very carefully, as fine emery and rough entered the soft surface of the cerium. Dry-polishing with a very fine file (the finest obtainable) was the most satisfactory way of preparing the sample. For the methods of measurement of the optical properties the reader is referred to the article on the subject by Ingersoll and Littleton⁴⁹ on "A New Method of Determining the Optical Constants of Metals." The constants determined on the magnesium-cerium alloys are given in the table below:

Per cent. cerium.	<i>n</i> .	<i>k</i> .
83	1.60	1.74
61	1.43	2.30
26	0.73	4.79
Pure Mg	0.32	12.0

CHEMICAL PROPERTIES OF METALLIC CERIUM.

Metal of approximately 98 per cent. cerium content was used in these determinations.

Cerium is very slightly attacked by cold water, but in boiling water a slow evolution of hydrogen gas occurs and the metal is tarnished black. At room temperature the following solvents have no action on cerium: ethyl alcohol, amyl alcohol, chloroform, carbon tetrachloride, concentrated sulphuric acid, concentrated ammonium hydroxide, concentrated sodium hydroxide. Ethyl ether has a very slight action on the metal, as have also 3 per cent. and 30 per cent. hydrogen peroxide at room temperature. The action of dilute sulphuric acid, concentrated and dilute hydrochloric acid, concentrated and dilute nitric acid, in the cold, is moderately vigorous. Ammonium chloride and potassium chloride, at room temperature, have moderate action on the metal. This may be explained by the fact that in water a small amount of cerium hydroxide forms which is soluble in potassium chloride and ammonium chloride, thus causing fresh surface of the metal to be exposed and resulting in moderate attack of the metal by the solvent. At boiling temperature the following solvents did not attack the metal, chloroform, carbon tetrachloride, concentrated sulphuric acid, concentrated ammonium hydroxide. The metal was only slightly attacked by the following solvents at boiling temperature: ethyl alcohol, amyl alcohol, ethyl ether and concentrated sodium hydroxide. Dilute nitric acid, ammonium chloride, potassium chloride and 3 per cent. hydrogen peroxide at boiling temperatures gave moderate action. Dilute sulphuric acid, concentrated and dilute hydrochloric acid, concentrated nitric acid and 30 per cent. hydrogen peroxide gave vigorous evolution of gas at boiling temperature.

The action of various gases on cerium was studied. A small amount of cerium filings was placed in a porcelain boat in a hard glass tube. The air was displaced by the gas under test, and the tube heated gently by means of gas burners. The cerium filings heated in chlorine emitted a very bright light at a temperature of 210° to 215° C. The salt formed

was tested and found to be anhydrous cerous chloride.

In bromine, cerium burned at a temperature of 215° to 220° C. with emission of less light than in the case of chlorine. The salt formed in solution in water, and was identified as the bromide.

In iodine vapors no light was emitted, although the tube was heated to a temperature of 300° C. On examination of the contents of the tube it was found that some iodide had formed.

Cerium burned with luminescence when heated in air to a temperature of 160° C. If a lump of cerium is sealed in a glass bottle and kept warm for some time, a black powder is seen to form upon the surface of the cerium, and when the bottle is opened this powder ignites at room temperature. This is probably due to the formation of a highly pyrophoric suboxide of cerium.

When cerium filings are heated to 345° in hydrogen gas, the hydride forms without emission of light. The hydride has been described and studied by Muthmann.⁵⁰

Cerium filings were heated in nitrogen to a temperature of 1000° C. No luminescence was observed, but some nitride was formed. This nitride is a black powder, and has been studied and described by Matignon.⁵¹

When the nitride is heated in potassium hydroxide solution, evolution of ammonia gas occurs. When exposed to air the nitride gradually changes over to a brown oxide.

Cerium filings were heated in the vapors of sulphur. When the black substance which is formed is treated with dilute sulphuric acid, sulphuretted hydrogen is evolved. Cerium sulphide has been studied by various investigators.⁵²

Cerium filings were heated to a temperature of 500° C. in an atmosphere of carbon monoxide. There was no visible reaction, but part of the filings appeared oxidized.

ALLOYS.

A number of different alloys of cerium were studied, and are described below. In most cases the alloys were high in cerium, usually containing about 70 per cent. cerium. The metals were weighed out in the proper proportions, using from five to ten grams of cerium. The cerium was first melted in a small porcelain crucible under a layer of sodium chloride, and the other metal added in small pieces. The porcelain crucible was, of course, attacked by the cerium, but it was found that a thin layer of silicide of cerium forms, and this protects the crucible from further attack. The metal can in most cases be removed without breaking the crucible if care is exercised, and therefore one crucible serves for several melts. The silicide does not appear as a contaminant in the alloy. Porcelain crucibles were used except in cases where especially pure metal was desired, when magnesia crucibles were employed.

The work on the alloys of cerium is presented below in an epitomized form. The time at the writer's disposal was such that a complete study of each alloy could not be made. However, specimens of all the

alloys described have been preserved and will be used for future references.

Silver.—Silver alloys with cerium quietly, and the thermal change appears to be small. The alloy has a silvery-white luster, and is hard and brittle. From all appearances, a compound is probably formed between cerium and silver.

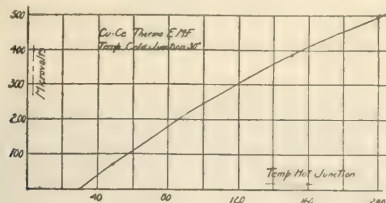


Fig. 10.

Gold.—When gold was added to molten cerium there was a slight flash from the crucible, but the reaction was not violent. The alloy was fairly soft, and had a reddish appearance. It disintegrated somewhat on aging, forming a purplish black powder.

Platinum.—The reaction between cerium and platinum appeared to be endothermic. The alloy was fairly hard and was pyrophoric. It disintegrated to a slight extent when aged.

Copper.—The cerium-copper alloy was hard and brittle, although the two component metals were soft and malleable. A compound is probably formed. The alloy disintegrated to a powder.

Tin.—This alloy was formed with the evolution of much heat. When first made, the alloy was pyrophoric, but on standing for a few months a powder formed, showing that the alloy disintegrated slowly when exposed to the air.

Antimony.—There was considerable evolution of heat on the formation of this alloy. The alloy was very soft and was non-pyrophoric. It did not oxidize nor disintegrate on aging.

Arsenic.—The reaction appeared to be exothermic. The alloy was fairly soft and somewhat pyrophoric. It did not decompose on being kept.

Carbon.—Carbon and cerium combine directly when heated together. The carbide has been referred to and described earlier in this article.

Silicon.—Cerium and silicon form the silicide CeSi_2 . This compound may be formed by the reduction of the oxide of cerium. Large amounts of the mixed silicides have been prepared by the writer. The following mixture is recommended for their preparation:

	Grams.
MgO_2	1,000
Powdered graphite.....	200
Powdered silicon.....	450

The silicide of cerium is somewhat brittle, and may easily be pulverized to a fine powder. It is a splendid reducing agent. When the silicide is added to cerium so that the silicon content is about 15 per cent. a good pyrophoric alloy is obtained.

Sulphur.—The preparation of the sulphide has been referred to earlier in this article.

Selenium.—Some reference is found in the literature to the selenide of cerium. Mosander reduced the

selenite in a stream of hydrogen and obtained a brown substance of a disagreeable odor. Moissan has shown that the selenides may be obtained by the action of selenium fumes on cerium carbide.

Selenium was added to molten cerium. The reaction was very vigorous, and was accompanied with the evolution of reddish fumes. The melt consisted of two portions, a powder and a metallic alloy. The powder was impure cerium selenide, and the alloy, which was pyrophoric, apparently consisted of the selenide dissolved in excess cerium.

Tellurium.—No reference was found in the literature to the telluride of cerium. Tellurium combined vigorously with molten cerium, giving a brownish pulverulent mass, which was probably the impure telluride. When treated with dilute acids, the well-known odor of hydrogen telluride was detected.

Lead.—When lead was added to molten cerium, a violet reaction occurred, causing a portion of the contents to be ejected from the crucible. The alloy was very soft, and emitted sparks of a reddish color when scratched with a file. The alloy disintegrated slightly on aging.

Calcium.—Calcium alloyed with cerium quietly, without evolution of much heat. The alloy was white and was harder than either constituent. When scratched with a file it emitted a cluster of bright sparks. It is stable in air, oxidizing very slowly. The alloy did not disintegrate.

Sodium.—Sodium alloyed with cerium quietly. The alloy was hard and slightly pyrophoric. It oxidized somewhat when exposed to air.

Aluminum.—Aluminum alloyed with cerium fairly quietly. The alloy was very hard and brittle. It disintegrated without oxidation. A compound of aluminum and cerium was probably formed. This alloy was not pyrophoric.

Zinc.—The combination of cerium and zinc was accompanied by a vigorous, in fact, almost explosive, reaction. There was a large amount of heat evolved. The alloy was hard, brittle and pyrophoric, and remained unoxidized when exposed to atmospheric conditions.

Cadmium.—Cadmium and cerium combined vigorously with considerable heat evolution. The alloy was hard, brittle and pyrophoric. On exposure to air a film of oxide formed slowly, but the alloy did not disintegrate.

Chromium.—The alloy was white in color, hard and brittle. It was somewhat pyrophoric. It remained unchanged in the air.

Manganese.—Manganese combined quietly with cerium, forming a fairly hard, pyrophoric alloy, stable in air.

Iron.—The iron-cerium alloys are very interesting, as they were the first pyrophoric alloys known, and were discovered by Dr. Auer von Welsbach. The alloys of about 70 per cent. cerium content are fairly hard and somewhat brittle. The microstructure of one of these alloys is shown in Fig. 11. It is seen that the structure is heterogenous, probably consisting in part of a cerium-iron compound. These alloys have been the subject of some discussion in the liter-

ature,⁵³ as have the reasons for the pyrophoric properties.⁵⁴ The writer believes that the question of the pyrophority depends upon the following factors: cerium alone is soft and malleable, and when scratched with a file, small particles are not broken off. However, when the alloy is hard and brittle, small particles are easily detached from the mass, and the friction is sufficient to raise the temperature of these small particles to the incandescent point of cerium (160°). As metallic compounds (such as Cu_3Sn) are as a rule hard and brittle, the addition of such compounds to cerium usually assures a pyrophoric alloy. The alloy should be high in cerium, so that ignition occurs at a low temperature, and should contain excess of cerium above that required for the formation of a compound (such as CeSi_2) to act as a binder and so prevent the disintegration of the alloy, as in the case of the cerium-aluminum alloy containing about 60 per cent. cerium.

Nickel.—The nickel-cerium alloys made were similar to the iron alloys, but were somewhat softer. The ones high in cerium were very pyrophoric.

Tungsten.—Powdered tungsten equivalent in weight to 15 per cent. was added to molten cerium. The tungsten dissolved fairly quickly and the reaction was quiet. The alloy was hard, brittle and pyrophoric.

Mercury.—Cerium forms amalgams fairly easily. Their preparation has already been described under the methods of purification. The amalgams containing only 1 or 2 per cent. of cerium are liquid, but the ones of higher percentage are solid. These amalgams oxidize easily in the air, and those containing 8 or 10 per cent. cerium take fire in the air.

Magnesium.—The whole series of these alloys were prepared, and have been discussed under optical properties. The alloy containing about 83 per cent. cerium is highly pyrophoric. Most of these alloys are brittle and can be easily pulverized. Excellent flashlight powders can be prepared from the ones of higher cerium content. These alloys also form splendid reducing agents, as the combination of cerium and magnesium is an endothermic reaction, and when the alloy is oxidized, more heat is emitted than from an equivalent mechanical mixture of the two constituents. The fact that the alloys of from 60 to 75 per cent. cerium content may be easily pulverized in a mortar to a fineness of 200 mesh should render these alloys valuable for thermal reductions. A small amount of metallic vanadium was prepared by reducing V_2O_5 by this method. The alloys of from 75 to 85 per cent. cerium content can be pulverized, but they are so highly pyrophoric that it is difficult to prevent igniting them.

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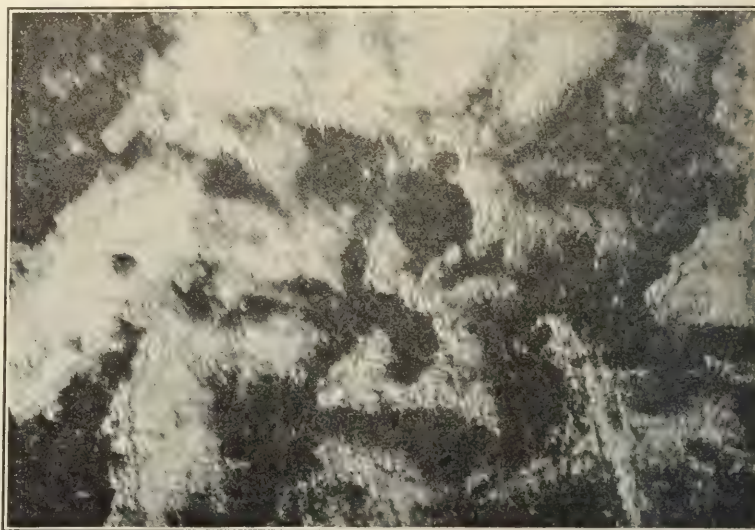


Fig. 11.

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ON THE DENSITY OF SILICATE MIXTURES.

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It has been shown by Winkelmann and Schott¹ that the densities of a glass may be calculated, with a rough degree of accuracy, from its chemical composition. The method depends upon the supposition that the several glass-forming oxides have densities which are always the same, for a particular oxide, in whatever combination it occurs. On this assumption, by addition of the partial volumes of the oxides, the densities of the glasses were calculated, according to the following equation,

$$(1) \quad \frac{a_1}{z_1} + \frac{a_2}{z_2} + \frac{a_3}{z_3} = \frac{100}{S},$$

where S is the density of the glass, a_1 , a_2 , a_3 are the percentages of the oxides, and z_1 , z_2 , z_3 are the densities of the oxides in the glass.

That this assumption is not entirely fulfilled is shown in the original article by the values of the densities for twenty-nine glasses calculated by this method. However, the average variation of 1 $\frac{1}{2}$ per cent., between the observed and calculated values does not militate against the method's value where extreme accuracy is not required.

In order that the factors used by Winkelmann might be checked against the more recent and accurate work in pure silicates, they were employed in calculating the densities of a series of calcium and magnesium metasilicates, described by Larsen,² two series of lithium-barium and lithium-calcium metasilicates, described by Wallace,³ and some mixed feldspars prepared by Day and Allen.⁴

The observed and calculated densities of the calcium-magnesium silicates are given in Table I. It is evident from these figures that Winkelmann's factors gave a fair value for the density of magnesium silicate, but a false value for calcium silicate. This is shown graphically in Line II (Fig. 1). The observed density of calcium silicate is greater than that of magnesium silicate while the hypothetical, calculated, density of calcium silicate is less. New factors for CaO and MgO were then calculated from the values of the observed densities. Following are the two sets of factors which were employed:

¹ Winkelmann, *Ann. d. Phys. und Chem.*, **49**, 401 (1893); Winkelmann and Schott, *Ibid.*, **51**, 697 (1894); "Jena Glass and Its Industrial Applications," Hovestadt (English edition), p. 148.

² *Am. J. Sci.*, **28**, 263 (1909).

³ *Z. anorg. Chem.*, **63**, 1 (1909).

⁴ *Bull.* **31**, Carnegie Institute of Washington.

	Winkelmann.	Modified
SiO ₂	2.3	2.3
CaO	3.3	4.1
MgO	3.8	4.0

The densities of the several calcium-magnesium silicates computed with the aid of the modified factors are given in the last column of Table I and shown graphically in line I (Fig. 1). They show a far more satisfactory agreement with the observed densities, and since the errors throughout the entire series are less than one-half of one per cent., the densities assumed for the oxides in the glass may be considered to be nearly correct.

TABLE I.—CaOSiO₃-MgSiO₃.

CaSiO ₃ , per cent.	CaO, per cent.	MgO, per cent.	SiO ₂ , per cent.	Density.		
				Obs. ¹	Calc. ²	Calc. ³
100	48.20	00.00	51.80	2.904	2.698	2.920
95	45.80	2.01	52.19	2.899	2.700	2.910
85.26	41.09	5.91	53.00	2.891	2.701	2.897
74	35.70	10.43	53.87	2.881	2.706	2.879
64	30.84	14.43	54.73	2.872	2.709	2.863
60	28.92	16.04	55.04	2.859	2.711	2.855
53.64	25.85	18.59	55.56	2.854	2.713	2.848
40	19.28	24.06	56.66	2.834	2.718	2.829
30	14.46	28.07	57.47	2.821	2.722	2.815
10	4.82	36.09	59.09	2.780	2.730	2.787
5	2.41	38.10	59.49	2.777	2.733	2.780
0	0.00	40.10	59.90	2.758	2.735	2.773

When these factors were used for calculating the densities of some of the Jena glasses, the results were, in general, more satisfactory than those obtained with Winkelmann's factors. The following examples show the observed and calculated densities of several of these glasses.⁴

No.	Density.			Error. ² Per cent.	Error. ³ Per cent.
	Obs.	Calc. ²	Calc. ³		
3.....	2.424	2.42	2.424	0.2	0.0
6.....	2.585	2.52	2.543	2.5	1.6
10.....	2.518	2.51	2.545	0.3	1.0
34.....	2.378	2.34	2.350	1.6	1.2
Average.				1.15	0.95

The observed and calculated densities of the lithium-barium metasilicates and the lithium-calcium metasilicates are given in Tables II and III respectively and all shown graphically in Fig. 2. In his original communication Winkelmann gave no factor for lithium oxide, consequently the value employed in

TABLE II.—Li₂SiO₃-BaSiO₃.

BaSiO ₃ , Per cent.	Li ₂ O, Per cent.	BaO, Per cent.	SiO ₂ , Per cent.	Density.	
				Observed. ⁵	Calc. ³
0	33.30	00.00	66.70	2.61	2.63
10	29.97	7.18	62.85	2.70	2.74
20	26.64	14.36	59.00	2.80	2.87
30	23.31	21.53	55.16	2.91	3.00
40	19.98	28.71	51.31	3.17	3.14
50	16.65	35.89	47.46	3.38	3.31
60	13.32	43.06	43.62	3.50	3.48
70	9.99	50.24	39.77	3.77	3.69
80	6.66	57.42	35.92	4.02	3.91
90	3.33	64.60	32.07	4.19	4.16
100	0.00	71.78	28.22	4.44	4.44

¹ Larsen, *Am. J. Sci.*, **28**, 263 (1909).

² Using Winkelmann's factors.

³ Using modified factors.

⁴ Winkelmann and Schott, *Loc. cit.*

⁵ Wallace, *Z. anorg. Chem.*, **63**, 1 (1909).

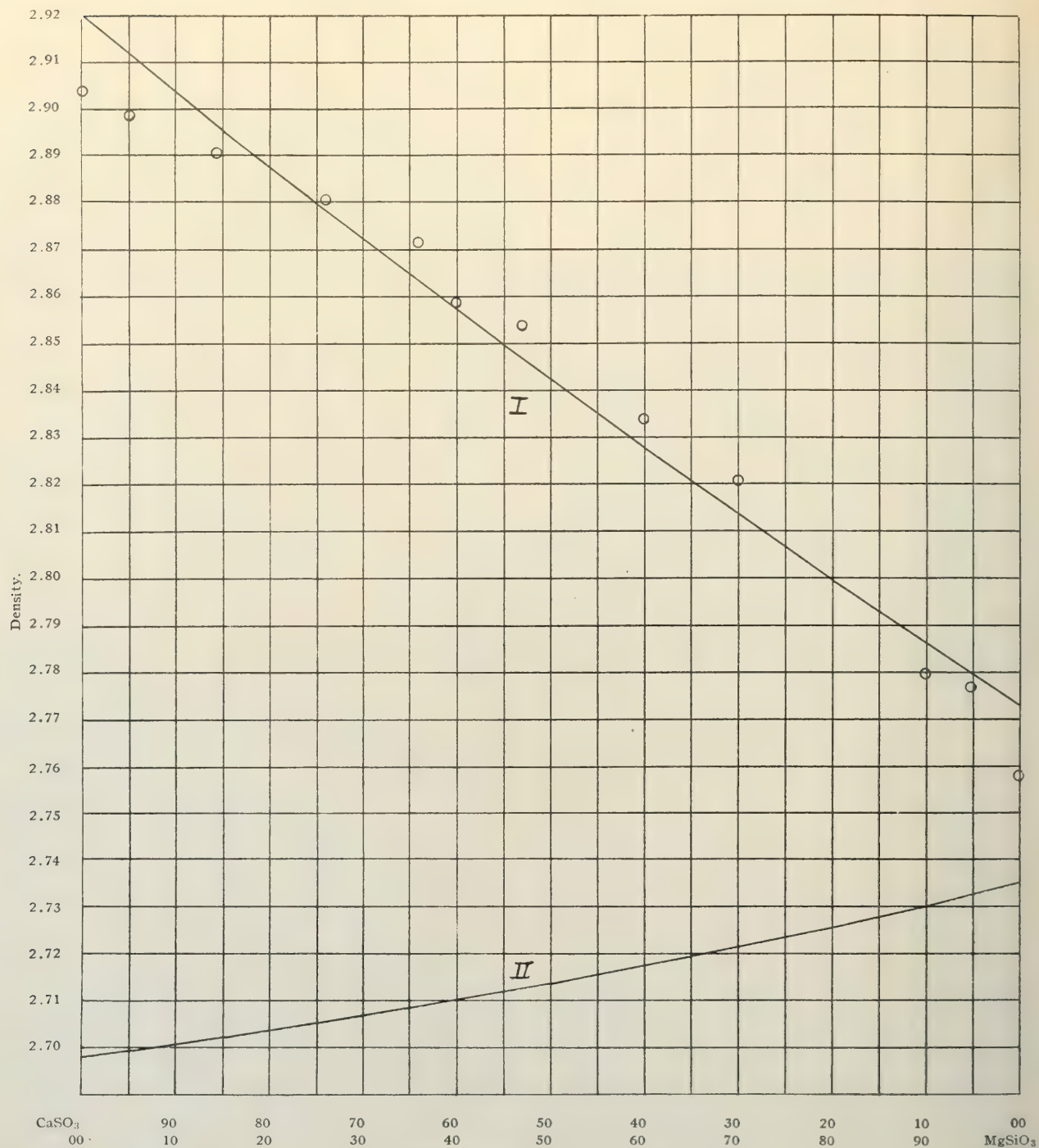


Fig. 1.

TABLE III.— $\text{Li}_2\text{SiO}_3\text{--CaSiO}_3$.

CaSiO ₃ Per cent.	Li ₂ O. Per cent.	CaO. Per cent.	SiO ₂ . Per cent.	Density.		
				Obs. ¹	Calc. ²	Calc. ³
0	33.30	00.00	66.70	2.61	2.63	2.63
10	29.97	4.82	65.21	2.64	2.63	2.65
20	26.64	9.64	63.72	2.69	2.645	2.69
30	23.31	14.46	62.23	2.72	2.655	2.71
40	19.98	19.28	60.74	2.76	2.66	2.74
50	16.65	24.10	59.25	2.80	2.665	2.77
60	13.32	28.92	57.76	2.80	2.67	2.80
70	9.99	33.74	56.27	2.84	2.68	2.83
80	6.66	38.56	54.78	2.85	2.69	2.85
90	3.33	43.38	53.29	2.88	2.69	2.88
100	0.00	48.20	51.80	2.91	2.70	2.92

these calculations is new so far as the writer is aware. The factors used in computing these densities are as follows:

	Winkelmann.	Modified.
SiO ₂	2.3	2.3
BaO.....	7.0	7.0
CaO.....	3.3	4.1
Li ₂ O.....	...	3.7

In the case of the lithium-barium series, Winkelmann's factor for BaO was found to give good results,

¹ Wallace, *Z. anorg. Chem.*, **63**, 1 (1909).

² Using Winkelmann's factors.

³ Using modified factors.

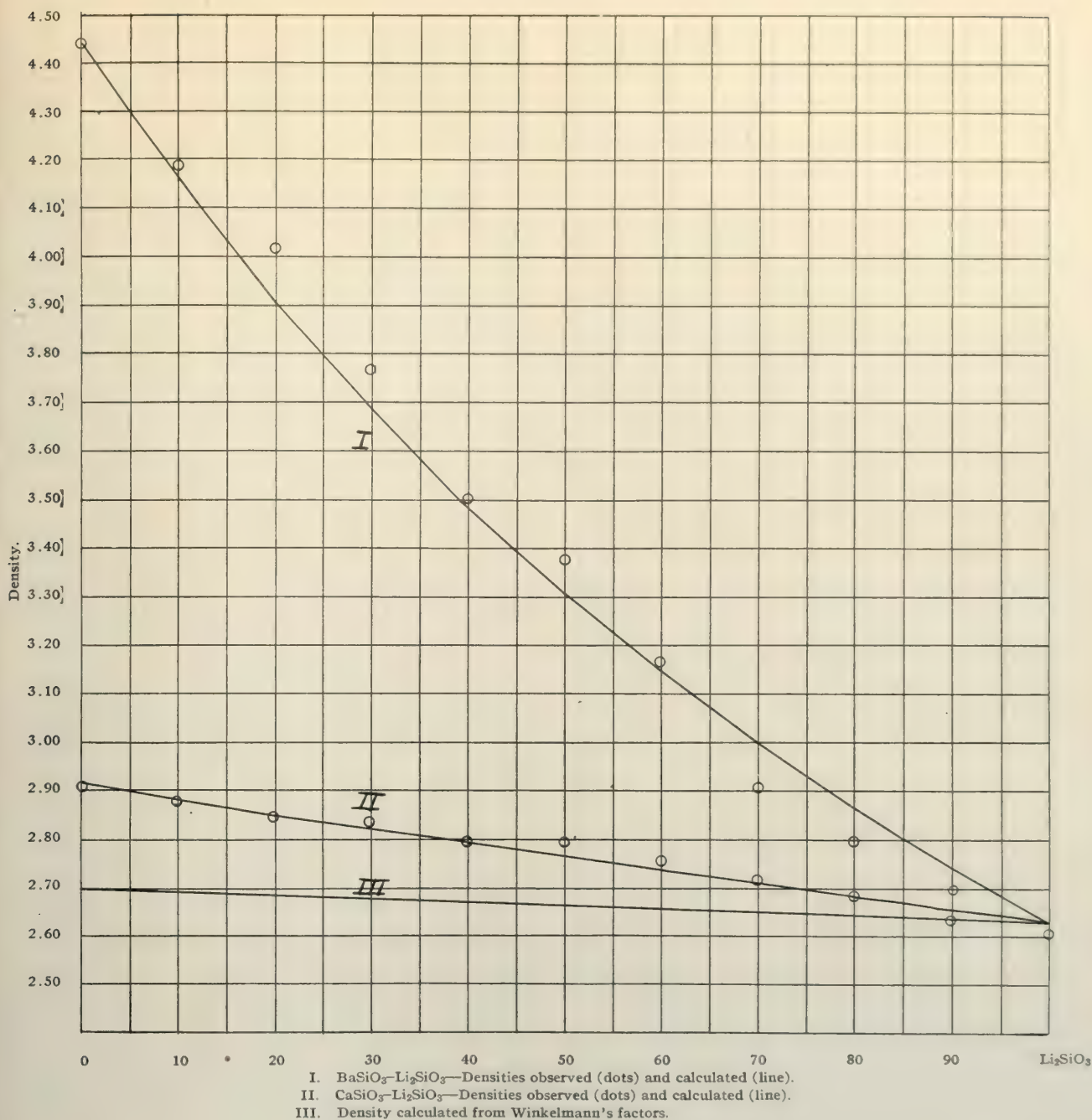


Fig. 2.

and was employed in the calculations. The error between the observed and calculated values of the density was comparatively large, however, but did not exceed in average of one and one-half per cent. A much better agreement exists between the observed and calculated densities of the lithium-calcium silicates. In this case the average error is less than one-half of one per cent., and is doubtless as satisfactory as could be expected of the method.

In Table IV is recorded a similar comparison of the observed and computed densities of several mixtures of albite and anorthite.¹ From the values given in this table, it is evident that the densities employed by Winkelmann give false results. The figures given

¹ Day and Allen, *Loc. cit.*

TABLE IV.—ALBITE-ANORTHITE.

	SiO_2	Al_2O_3	CaO	Na_2O	Density:		
					Obs. ¹	Calc. ²	Calc. ³
An.....	43.33	36.60	20.06	0.11	2.700	2.980	2.700
An ₂ Ab.....	47.10	34.38	17.00	1.74	2.648	2.880	2.644
An ₃ Ab.....	51.06	31.72	13.65	3.68	2.590	2.820	2.600
An ₁ Ab ₂	60.01	25.24	7.09	7.79	2.486	2.680	2.497

in the last two columns of Table IV were calculated with the aid of the following factors:

	Winkelmann's.	Modified.
SiO_2	2.3	2.3
Al_2O_3	4.1	2.75
CaO	3.3	4.1
Na_2O	2.6	2.6

¹ Day and Allen, *Loc. cit.*² Using Winkelmann's factors.³ Using modified factors.

The value of the density of aluminum oxide, employed in these calculations, was checked against two Jena glasses¹ which contain large percentages of Al_2O_3 . The results are as follows:

No.	Observed.	Calc. ²	Calc. ³	Error. ² Per cent.	Error. ³ Per cent.
4.....	2.480	2.60	2.471	4.8	0.3
9.....	2.588	2.69	2.612	3.9	0.9
Average, 4.35				0.6	

In both cases the use of the new factors gives more accurate values for the densities.

These new factors present some interesting variations from those originally proposed. From the following table, which shows the old and new factors and the densities of the pure oxides, it appears, as Winkelmann observed, that the oxides in general show a higher density in the glass than in the uncombined condition.

	Winkelmann.	Modified.	Density of pure oxide.
CaO.....	3.3	4.1	3.316 ⁴
MgO.....	3.8	4.0	3.614 ⁵
Al_2O_3	4.1	2.75	3.85 ⁶
Li_2O	3.7	2.102 ⁶

Especial attention should be called to the condensation of lithium oxide which amounts to a seventy-five per cent. increase in density. Aluminum oxide appears to be an exception to this generalization and shows an expansion of 40 per cent. Although deductions may not be drawn from these figures, they appear to indicate a peculiar molecular condition, perhaps association, in the aluminum oxide, which is not characteristic of the other oxides in question.

Although these differences are interesting and suggestive, they are not truly indicative of real differences, since the method by which they are obtained rests upon incomplete assumptions. Only the oxides are considered and no account is taken either of the compounds which are present or of their constitution. That this is an important item in any theoretical relationship between the chemical composition of a substance and its density, or any other physical property, is well known in the case of organic compounds, and, even among the silicates, polymorphic forms⁷ of the same chemical composition, but of different density, have been described. A knowledge of the different compounds which exist, together with knowledge of the compounds which are stable at the temperature at which the glass may be formed, will aid materially in solving the numerical relationship between the chemical composition of a glass and its density. Until such information is at hand resort must be had to empirical factors which represent not the true density, but the true density plus or minus an element which is characteristic of the nature of the compound which is formed. Since, in all the pos-

sible mixtures of glass-forming oxides, the field in which glasses are formed is rather limited, the constitution of the more common glasses is more or less similar, and it therefore becomes possible to find factors which hold to a limited degree.

SUMMARY.

1. The density of some pure and mixed silicates have been calculated, using the method and factors suggested by Winkelmann and Schott, with unsatisfactory results.

2. New factors have been derived, which appear to be more satisfactory. These are CaO 4.1, MgO 4.0 and Al_2O_3 2.75.

3. A factor has been derived for lithium oxide, Li_2O 3.7.

4. Although the method is not theoretically correct, it is capable of giving, for large variety of glasses, results which are not more than one or one and one-half per cent. in error.

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THE DETERMINATION OF VOLATILE MATTER IN COAL.

By S. W. PARR.

Received October 6, 1911.

The variable results obtained in volatile matter determinations on coal have been ascribed to (a) mechanical loss and (b) to different forms of decomposition as a result of varying methods of applying heat. With lignites, as shown by Somermeier,¹ the first-named difficulty is especially pronounced; but we find also in this laboratory that there are numerous coals of the Illinois type which suffer mechanical loss to an appreciable extent when subjected to the usual method for volatile matter determination. This is evident from the sparks that frequently accompany the discharge of the volatile matter and seems also to be indicated by Table II, which gives values for ash as derived from the coke resulting from the official method of determining the volatile matter (column B) as compared with the ash as derived by the official method. In any study, therefore, of the effect of varying temperatures, it is essential that variations due to mechanical loss be first eliminated before conclusions can be safely drawn as to the effect of varying degrees of heat. Moreover, the method employed must admit of the application of the maximum of heat in the minimum space of time in order that variations due to different sorts of decomposition may be brought within a narrow range. This precludes, of course, the application of a slow preliminary heating as suggested for lignites, at least with Illinois coals.

In our experiments it has seemed well to bear in mind certain other sources of variation. First on account of the great avidity of freshly mined coal for oxygen, it is possible that this element, mechanically held or absorbed by the finely ground material, accentuates or adds to the normal content of oxygen

¹ Winkelmann and Schott, *Loc. cit.*

² Using Winkelmann's factors.

³ Using modified factors.

⁴ Day and Shepherd, *Am. J. Sci.*, [4] **22**, 265 (1906).

⁵ Larsen, *Ibid.*, [4] **28**, 273 (1909).

⁶ Van Nostrand's Chemical Annual.

⁷ "The Lime-silica Series of Minerals," Day and Shepherd, *J. Am. Chem. Soc.*, **28**, 1089 (1906). "Minerals of the Composition Mg_2SiO_5 : A Case of Tetramorphism," Allen, Wright and Clement, *Am. J. Sci.*, [4] **22**, 385 (1906).

¹ *J. Am. Chem. Soc.*, **28**, 1003 (1906).

of the crucible and may thus furnish an initial oxidation of appreciable amount. To guard this point and at the same time prevent mechanical loss, numerous experiments were undertaken wherein a liquid was added to the dry coal which would have non-oxidizing properties and whose vapor would tend to carry out the oxygen content of the crucible at a temperature below that where oxidation would begin and at the same time promote adhesion and prevent the blowing out of the particles as a result of the moistening throughout of the mass. Such a liquid, of course, must be completely volatile and be distilled without decomposition by the subsequent heat.

TABLE I.—VOLATILE MATTER IN COAL.

Table No.	Lab. No.	Kind of coal.	A.	Variation	B.	Variation
			Standard method.	+ or — from av., Column A.	Standard with kerosene.	+ or — from av., Column B.
1	117	Vermilion Co., Ill.	38.90	+0.21	38.40	+0.07
			38.48	—0.21	38.26	—0.07
			Average,	38.69	0.21	38.33
2	128	Saline Co., Ill.	36.41	—0.14	36.61	—0.03
			36.69	+0.14	36.68	+0.04
			Average,	36.55	0.14	36.64
3	214	Lignite, Mississippi.	47.09	+1.06	44.87	+0.58
			45.70	—0.33	44.35	+0.06
			45.25	—0.78	43.95	—0.34
			46.09	+0.06	43.99	—0.30
			Average,	46.03	1.11	44.29
4	1762	Sangamon Co., Ill.	40.48	—0.74	40.05	+0.01
			41.72	+0.50	40.03	—0.01
			41.67	+0.45
			41.00	—0.22
			Average,	41.22	0.95	40.04
5	1809	Williamson Co., Ill.	37.24	+0.03	37.41	—0.05
			37.18	—0.03	37.52	+0.06
			Average,	37.21	0.03	37.46
6	1810	Franklin Co., Ill.	34.65	—0.32	34.78	+0.10
			35.30	+0.33	34.59	—0.09
			Average,	34.97	0.32	34.68
7	1870	Christian Co., Ill.	41.12	+0.68	39.41	+0.10
			39.76	—0.68	39.21	—0.10
			Average,	40.44	0.68	39.31
8	1878	Jackson Co., Ill.	34.32	—0.12	34.72	+0.19
			34.55	+0.11	34.70	+0.17
			34.43	—0.10
			34.26	—0.27
			Average,	34.42	0.11	34.53
9	2902	Williamson Co., Ill.	33.29	—0.18	33.78	0.00
			33.65	+0.18	33.77	0.00
			Average,	33.47	0.18	33.77
10	4035	Sangamon Co., Ill.	40.47	+0.07	41.35	+0.01
			41.33	—0.07	41.33	—0.01
			Average,	41.40	0.07	41.34
11	4085	Vermilion Co., Ill.	35.85	—0.08	36.54	—0.04
			36.01	+0.08	36.63	+0.05
			Average,	36.93	0.08	36.58
12	4130	Franklin Co., Ill.	37.06	+0.05	36.72	+0.16
			36.96	—0.05	36.41	—0.15
			Average,	37.01	0.05	36.56
Average variation,			0.33		0.13	

Numerous vehicles were tried, such as ether, alcohol, carbon tetrachloride, petroleum ether, kerosene, etc. Of these substances, kerosene seemed to be the best adapted, besides being readily available. The procedure was very simple. One gram of the air-dried sample, ground to 80 mesh, was weighed into the crucible and ordinary kerosene, from 10 to 15 drops, added, sufficient in amount to completely penetrate and saturate the coal. The cover was then put in place, the crucible supported on a platinum or nichrome triangle and placed directly in the usual Bunsen flame, 20 cm. high as prescribed by the Committee on Coal Analysis.

The results of a number of determinations are given in Table I, along with results obtained by the official method.

The values at the foot of the columns indicated that by the use of kerosene the variations are reduced from an average of 0.33 per cent. to 0.13 per cent.

As further evidence tending to show absence of mechanical loss when kerosene is applied, the results in Table II show the ash as obtained by the official method in column A, with which may be compared column C, showing the results for ash as derived from the coke obtained when kerosene was added as above described.

TABLE II.—MECHANICAL LOSS AS INDICATED BY ASH DETERMINATIONS.

Table No.	Lab. No.	Kind of coal.	A.	B.	C.
			Ash by official method.	Ash from coke residue by official method.	Ash from coke residue using kerosene.
1	117	Vermilion Co., Ill.	8.74	8.66	8.82
2	1162	Christian Co., Ill.	11.32	11.15	11.26
3	2902	Williamson Co., Ill.	10.12	9.75	10.07
4	2952	Pittsburg, Pa.	16.95	16.92	16.89
5	4035	Sangamon Co., Ill.	9.44	9.31	9.40
6	4085	Vermilion Co., Ill.	23.58	23.70	23.50
7	4130	Franklin Co., Ill.	4.87	4.79	4.80

It seems fair to conclude, therefore, that an advantage attends the use of kerosene and that the matter of mechanical loss is thereby eliminated. This brings us to a consideration of that phase of the matter which relates to variations due to differences in the application of heat. Fieldner and Davis¹ have shown that variations in heat as derived from burners of different sizes, different types of gas, etc., yield different values. Their discussion of the results would lead one to infer that in their opinion the various temperatures employed produced a varying speed of decomposition which resulted in the fixation of varying amounts of carbon. With bituminous coals at least it would seem essential to first eliminate the possibility of mechanical loss. But, aside from this feature of the case, there are many evidences that in the main the variations due to different temperatures are the result of a more or less complete driving off of the residual hydrogen, to variations in the amount of carbon deposit on lid and sides of the crucible, to the oxidizing or reducing character of the flame immediately above and around the lid of the crucible, the extent of leakage or care with which the lid of the crucible is made to fit, etc.

¹ THIS JOURNAL, 2, 304 (1910).

Further uniformity of results might be expected if we could locate more precisely the point wherein the variation occurs. This feature of the case is receiving further study.

As bearing somewhat on the case, the following table is submitted. If any interpretation can be attempted from these results it would seem to be that the higher results are not always to be credited to the larger burner and the higher temperature. It is more likely that coals vary as to the ease or completeness with which they part with their last residuum of gas.

I am indebted to Mr. F. W. Whittum and Mr. J. M. Lindgren for the analytical results accompanying this paper.

TABLE III.

Table No.	Lab. No.	Kind of coal.	A. Standard method with kerosene burner.	B. Standard method with Fletcher burner.	B compared with A variation + or -.
			Sargent burner.	Fletcher burner.	
1	117	Vermilion Co., Ill.	38.33	39.44	+1.11
2	128	Saline Co., Ill.	36.64	37.11	+0.47
3	214	Lignite, Mississippi.	44.29	44.35	+0.06
4	1762	Sangamon Co., Ill.	40.04	39.84	-0.20
5	1809	Williamson Co., Ill.	37.46	37.78	+0.32
6	1810	Franklin Co., Ill.	34.68	35.18	+0.50
7	1870	Christian Co., Ill.	39.31	39.65	+0.34
8	1878	Jackson Co., Ill.	34.53	34.22	-0.31
9	2902	Williamson Co., Ill.	33.77	34.16	+0.39
10	4083	Vermilion Co., Ill.	36.58	36.29	-0.29
11	4130	Franklin Co., Ill.	36.56	36.99	+0.43

In column A, the burner used is illustrated as No. 1000 in Sargent's catalogue. It has an internal diameter of 9 mm.

In column B, the Fletcher burner had an internal diameter of 11 mm.

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SOME NEW FEATURES IN THE ELECTROLYTIC DETERMINATION OF LEAD.

By JOHN G. FAIRCHILD.

Received Sept. 28, 1911.

It has been found that good deposits of lead peroxide, free from flakes and of close texture, can be obtained on a smooth platinum cylinder in two hours' time without rotation, and as much as 100-200 mg. in weight. This can be raised to 300 mg. but there is danger of flaking off. The secret of success is a low amperage to begin with and a hot solution, 50°-60° C.

For alloys high in lead two grams or more are weighed out and an aliquot taken to represent about 0.1 gram of metallic lead. The volume of electrolyte is 200 cc. in a 250 cc. beaker, and contains 30 cc. strong HNO₃. Heat to 50°-60° C., using an anode of 25 sq. in. surface with a cathode cylinder of 12 sq. in. The anode should be burnished frequently and ignited previous to placing in the electrolyte. This ignition removes any greasy film adhering to the cylinder. Split cover glasses are used to prevent loss through

evaporation of the hot solution, which just completely immerses the edge of the anode cylinder. The current is started at 0.25 am. for one hour and a half when it is raised to 0.5 am. for half an hour longer to remove the last traces of lead, and the cover glasses are rinsed down. At the end of two hours deposition is complete, as shown by the newly immersed stem remaining bright. The beaker is lowered and removed, being replaced by one containing clean water for rinsing the cylinders, which are then disconnected, the anode being rinsed in a glass of alcohol, drawn through a flame to burn off what adheres while holding the cylinder in a vertical position. It is then held for a few seconds about a foot above the flame to dry thoroughly, and weighed. On adding ammonia to the electrolyte and passing H₂S, no more than a mere brownish color should show.

To prove the accuracy of this method, purified lead sulphate was taken as the standard. An amount equal to 0.7335 gram was put into a 500 cc. flask and dissolved in just enough hot am. acetate solution, 100 cc. being taken for analysis by means of a pipette standardized to the flask. After adding 30 cc. HNO₃, of 1.42 sp. gr., this aliquot was made up to 200 cc. The electrolyte is best kept hot throughout the run by means of a hot plate or burner. The results for lead sulphate and test lead were as follows:

PbSO ₄ .	PbO ₂ equiv.	PbO ₂ found.	Pb. Per cent. ¹
0.1467	0.1157	0.1156	99.92
0.1467	0.1157	0.1160	100.26
0.1467	0.1157	0.1155	99.83
0.1467	0.1157	0.1159	100.17
Test lead.			
0.1000	0.1157	0.1145	98.92
0.1000	0.1157	0.1143	98.72
0.1000	0.1157	0.1142	98.63
0.1000	0.1157	0.1147	99.14
0.1000	0.1157	0.1145	98.92
0.1000	0.1157	0.1146	99.04

Whenever a weight was low the lead was found to be not all deposited, due to faulty manipulation which is not likely to occur. If the electrodes short-circuit re-solution occurs with some lead flaking off.

Lead scrap and furnace dross can be treated thus: About 5 grams are dissolved in HNO₃ + H₂SO₄ in a Kjeldahl flask and evaporated till fumes appear. After cooling, the impure PbSO₄ is filtered off, the paper punctured and the precipitate rinsed back into the flask. It is then treated with just sufficient hot saturated am. acetate solution, which is warmed till solution is complete, then filtered into a 500 cc. flask, a proper portion being taken for electrolysis.

On comparison with pure lead it will be seen that material relatively low in lead will require only about half an hour at 0.5 am., a small percentage of lead being given a higher amperage. In this way can lead be readily separated from copper, manganese, silver, antimony, etc.? When a relatively large amount of copper is present, as in blister copper, only 20 cc. nitric acid may be present. The presence or absence of am. nitrate seemed to have no effect on the results.

This method gives lower results than the chromate method; thus, by the latter 59.25 per cent. lead was

¹ Conversion factor 0.866.

found in a lead dross, by the electrolytic 58.85 per cent. On a copper matte high in lead, the figures gave 10.57 chromate, 10.32 electrolytic.

Material such as a copper matte can be dissolved in HNO_3 , the sulphur globule oxidized by adding KClO_3 crystals, then heated with H_2SO_4 till fumes come off.

The voltage of the hot solution is 2-2.5 volts. A straight platinum wire was first tried as cathode but metallic lead deposited on it. Also, with 1 ampere of current metallic lead deposits on the cathode. Even with a weak current in a cold solution there is danger of metallic lead separating. Results are best obtained with a low voltage and low current density.

In the early experiments, whenever lead sulphate was involved, this was changed to carbonate by digestion with ammonium carbonate, and the lead carbonate was dissolved in dilute nitric acid. These steps were soon found to be unnecessary, the simple solution of the lead sulphate in am. acetate greatly shortening the method.

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WASHINGTON, D. C.

NAPHTHALENE IN ROAD TARS. I. THE EFFECT OF NAPHTHALENE UPON THE CONSISTENCY OF REFINED TARS.

By PREVOST HUBBARD AND C. N. DRAPER.
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Naphthalene, C_{10}H_8 , often occurs in coal tar in larger quantities than any other one hydrocarbon and for this reason it is natural to suppose that it exerts an appreciable influence upon the quality and applicability of coal tars used as road binders. In this country the use of tars in road treatment and construction has advanced rapidly during the past few years and upon the market to-day are to be found a number of tar preparations intended for such use. These preparations are as a rule made by distilling off the lighter and more volatile constituents from both crude coal tar and crude water-gas tar or mixtures of the two. The residual products, which vary in consistency according to the extent and method of distillation, are sold for road purposes. Many successes and many failures have resulted from the use of coal tar and water-gas tar road binders, and often no clew has been obtainable as to the reason for such diverse results. In view of this fact, a systematic study of the principal chemical constituents of road-tar preparations and their effect upon the quality of such preparations is now being made in the laboratories of the Office of Public Roads, United States Department of Agriculture.

In the present paper, which is the first of a series upon naphthalene, no attempt will be made to review the chemistry of this substance, since this discussion is reserved for a later publication which will cover the entire subject as presented in the individual papers. A few remarks concerning certain physical properties

of naphthalene may, however, not be amiss at this point.

Naphthalene, in the pure state, exists in white crystalline masses of thin rhomboidal scales melting at 79°C . and having a boiling point of 218°C . Its specific gravity at 15°C . is 1.1517. It has a very characteristic odor, commonly familiar in moth balls, and is extremely volatile, considering its high molecular weight, so much so that in the manufacture of coal gas it is only partially deposited in the condensers, while the remainder is carried into the purifiers and into the gas mains, where it deposits in the bends of pipes during cold weather and often causes them to become clogged. Naphthalene volatilizes far below its boiling point and, in crude tars, distills to a considerable extent with aqueous vapor and also with the light tar oils, which accounts for its occurrence in the first fractions. Even at ordinary temperatures, it volatilizes slowly and gives off a penetrating tarry odor. It is slightly soluble in hot water, but dissolves easily in alcohol, ether, fatty and essential oils, acetic acid, and especially in the phenols and lighter tar distillates. No entirely satisfactory method for the quantitative determination of naphthalene in tar has, as far as the authors are aware, been devised up to the present time, although methods have been put forth by various investigators for the determination of naphthalene in illuminating gas.

It is a rather generally accepted theory that, in the manufacture of coal gas, the formation of naphthalene is due to certain complex reactions which take place only at the high temperatures at which the retort is maintained in modern gas-house practice. According to Cooper,¹ "a few years ago—when lower temperatures were in vogue, and when lower makes per ton of coal carbonized were registered—naphthalene was an almost unknown quantity; but now that the stress of competition demands the highest possible output of gas, it seems also to bring in its train the formation of large quantities of naphthalene." It is certain, however, that other factors, such as the size, shape, and inclination of the retort with relation to the volume of the charge of coal, and the varying conditions to which the evolved gases are subjected before and during their passage from the retort, have a great deal to do with the quantity of naphthalene formed.

Tars used as road binders are for the most part soft pitches obtained by distilling from 15 to 30 per cent. of the lighter products from the crude material. The soft pitch contains a large proportion of the naphthalene which may have been present in the original tar, and it is the study of the effect of naphthalene upon this grade of material that is the subject of this paper. As consistency is one of the most important properties of a road tar, it was thought well first to investigate the effect of varying percentages of naphthalene upon a given tar.

From its very nature naphthalene itself can be considered as a binding material. For some time past it has been known, however, to serve as a flux

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¹ *J. Gas Light.*, 110, 498 (1910).

for the binding constituents of tars, in spite of the fact that it is a crystalline solid. Thus it is possible to combine, by heating together, a hard tar pitch and a quantity of naphthalene with the formation of a soft product. It was thought, therefore, that a comparison of its fluxing value with that of certain less volatile tar distillates would prove most instructive. For this purpose a representative coal tar was taken and distilled to 238°C . in order to remove all the naphthalene. This naphthalene-free tar pitch, which was used for the following tests, was so hard that it was difficult to make an impression on it with the finger. An arbitrary measure of the consistency of this pitch was then obtained by means of the New York Testing Laboratory float-test apparatus, which is customarily used for this purpose in the routine examination of tar products in the Office of Public Roads.¹

The float apparatus, briefly described, consists of an aluminum float or cup, $3\frac{1}{2}$ inches in diameter, into which is screwed a small brass conical collar or mold. This collar is $\frac{7}{8}$ inch high, with an internal diameter at the top of $\frac{3}{8}$ inch and at the bottom of $\frac{1}{2}$ inch.

In making the test the brass collar is placed with the small end down on a brass plate which has been previously amalgamated with mercury by first rubbing it with a dilute solution of mercuric chlorid nitrate and then with mercury. A small quantity of the material to be tested is heated in a metal spoon until quite fluid, with care that it suffers no appreciable loss by volatilization and that it is kept free from air bubbles. It is then poured into the collar in a thin stream until slightly more than level with the top. The surplus may be removed after the material has cooled to room temperature, by means of a spatula blade which has been slightly heated. The collar and plate are then placed in a tin cup containing ice water maintained at 5°C . and left in this bath for at least 15 minutes. Meanwhile another cup is filled about three-fourths full of water, placed on a tripod, and the water heated to any temperature at which it is desired to make the test. This temperature is accurately maintained, and is at no time throughout the entire test allowed to vary more than one-half a degree centigrade from the temperature selected. After the material to be tested has been kept in the ice water for at least 15 minutes, the collar and contents are removed from the plate and screwed into the aluminum float, which is then immediately floated in the warmed bath. As the plug of bituminous material becomes warm and fluid it is gradually forced upward and out of the collar until water gains entrance to the float and causes it to sink.

The time in seconds between placing the apparatus on the water and when the water breaks through the bitumen is determined by means of a stop-watch and is taken as a measure of the consistency of the material under examination. Results so expressed are only relative, but they are comparable to within a good degree of precision. The temperature at which

the water bath is maintained is purely an arbitrary matter and, for routine work in the office, 32°C . and 50°C . have been selected as a matter of convenience when testing the comparatively soft and comparatively hard road tars.

For the work described in this circular 55°C . and 80°C . were adopted as most convenient temperatures. The former was selected after making a series of float tests upon the prepared coal tar pitch at temperatures varying from 40°C . to 60°C . In these tests it was found that at 40°C . and 45°C . the tar had not softened sufficiently to complete the test at the end of 1 hour; at 50°C . a test of 24 minutes and 18 seconds was obtained; at 55°C ., 9 minutes and 47 seconds; and at 60°C ., 3 minutes and 45 seconds. The duration of the test at 55°C . seemed most satisfactory as allowing sufficient leeway for comparative results without consuming too much time. It was decided to select 80°C . as a second working temperature, as it was the nearest convenient one to the melting point of naphthalene. It was thought that, by making consistency tests upon the naphthalene tar-pitch mixtures, later described, at both 55°C . and 80°C ., the results would show not only how much the mixture softened at the higher temperature, but what differences, if any, might be due to naphthalene below and above its melting point.

When the matter of temperatures had been decided upon and the consistency of the pitch had been determined at these temperatures, naphthalene mixtures were made as follows: Approximately 30-gram samples were accurately weighed into a series of small tin dishes, and varying percentages of c. p. flake naphthalene were added, starting with 0.5 per cent. of naphthalene and gradually increasing this amount to the extent of 30 per cent. In all, 13 samples were prepared. Before adding the naphthalene, each weighed sample of tar was warmed in the tin dish until fairly fluid, after which the naphthalene was added and the mixture well stirred. It was found better to add the naphthalene a little at a time during the process of mixing rather than to add the entire amount at one time, as by so doing there was less danger of losing some of the naphthalene by volatilization and a uniform mixture was more readily obtained. As the naphthalene was added, an increase in the fluidity of the mixtures was readily seen. Where 20 per cent. of naphthalene was used, the mixture was found to be fluid at normal temperatures, whereas the original pitch was semisolid. The naphthalene combined with the tar with surprising readiness and, upon cooling, no traces of the naphthalene could be seen in the resulting mixture, except where high percentages were added. It was found, however, that between 15 and 20 per cent. of naphthalene caused the tar to become saturated. The 15 per cent. mixture was homogeneous when cold, but in the 20 per cent. mixture a small amount of naphthalene crystals separated out upon cooling. This fact indicates that the tar pitch forms a sort of eutectic with naphthalene similar to certain metallic alloys. Above the approximate eutectic of 20 per cent. the

¹ Bull. 38, 14-16, U. S. Dept. of Agriculture, Office of Public Roads.

naphthalene crystallized out more and more as the percentage was increased. A mixture of 30 per cent. of naphthalene solidified. This was due to the crystallization of the excess of naphthalene. The consistency of this mixture at 55° C. was found to be higher than the preceding mixtures, owing to the separation of the naphthalene, which does not melt at this temperature. At 80° C. the consistency of this mixture was *nil*; that is, it became very fluid, as would naturally be expected. The maximum increase of fluidity of the tar was obtained with 20 per cent. of naphthalene, which is practically the eutectic point. These facts will be noticed on the curves A and A' (Fig. 1), which show the consistency of the mixtures plotted against the varying percentage of naphthalene.

Curve A shows the decided effect which naphthalene has upon the tar at 55° C., and A' the effect at 80° C. As the temperature of the water bath during the float test is raised, the curve A will approach A' and a series of curves might be obtained, lying between A and A', for water-bath temperatures between 55° C. and 80° C.

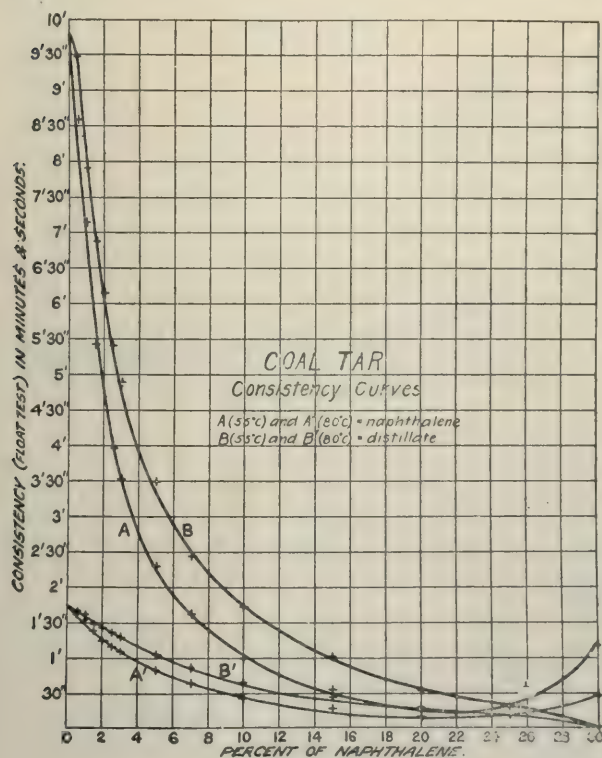


Fig. 1.

The sensitiveness of the tar pitch to small increments of naphthalene is shown by the sharp drop in the first section of curve A, starting with the addition of 0.5 per cent. of naphthalene, which increases the fluidity 1 minute and 12 seconds. The fluidity increases very markedly until 7 per cent. of naphthalene is reached, when the curve becomes more gradual, while increasing percentages of naphthalene have a much smaller effect. The curve drops, however, until 20 per cent. of naphthalene is reached and then rises gradually to 25 per cent. of naphthalene, owing

to the separation of naphthalene, as previously explained. At 30 per cent. of naphthalene a sharp rise is noted and the curve, if continued further, would rise almost perpendicularly, because the naphthalene is so much in excess that an accurate measurement of the consistency would be impossible. For reference to the percentage increase in fluidity, owing to increasing increments of naphthalene, the data given in Table I calculated from the curves will show statistically what the curves represent graphically.

TABLE I. PERCENTAGE INCREASE IN FLUIDITY OF COAL TAR PITCH, OWING TO ADDITIONS OF NAPHTHALENE AND NAPHTHALENE-FREE TAR DISTILLATE

Per cent. of naphtha- lene or distillate.	Due to naphthalene.		Due to distillate.	
	At 55° C. Per cent.	At 80° C. Per cent.	At 55° C. Per cent.	At 80° C. Per cent.
0.5	12.2	6.7	3.1	3.8
1.0	26.9	11.5	19.1	5.8
1.5	44.5	19.2	29.6	14.4
2.0	50.8	27.9	37.1	17.3
2.5	59.3	32.7	44.6	20.2
3.0	64.1	36.5	49.9	25.0
5.0	76.5	51.0	64.2	39.4
7.0	83.3	63.5	75.1	49.0
10.0	91.5	75.0	82.3	61.5
15.0	94.4	83.7	89.6	74.0
20.0	97.3	90.4	94.5	83.7
25.0	96.9	89.4	96.6	89.4
30.0	88.1	75.0	100.0	100.0

It will be observed that 7 per cent. of naphthalene increases the fluidity of the tar 83.3 per cent. at 55° C., while 20 per cent. increases it 97.3 per cent., showing that the additional 13 per cent. of naphthalene makes an increase of only 14 per cent. in fluidity. This fact is shown by the gradual slope of the curve A between these points as contrasted with the steep slope up to 7 per cent.

For comparison with the consistency results obtained with naphthalene, a portion of the original coal-tar pitch was saved for use in mixtures with a naphthalene-free tar distillate. Duplicate tests were carried out in the same way as were the naphthalene tests, except that equivalent percentages of a naphthalene-free distillate were employed. This distillate was a mixture of oils taken from the distillation of several water-gas tars and showed the following composition upon fractional distillation in an Engler flask:

TABLE II.—FRACTIONAL DISTILLATION OF TAR DISTILLATE.

Temperature in ° C.	Per cent. distilled.	Temperature in ° C.	Per cent. distilled.
Up to 190	0.7	Up to 280	47.5
Up to 200	1.0	Up to 290	55.5
Up to 210	1.8	Up to 300	62.5
Up to 220	5.0	Up to 310	71.0
Up to 230	7.5	Up to 320	77.5
Up to 240	14.5	Up to 330	83.0
Up to 250	23.0	Up to 340	89.0
Up to 260	28.5	Up to 346 ¹	94.0
Up to 270	37.0		

The specific gravity of this distillate was 1.006 at 25° C. and, upon cooling to -10° C., no solids crystallized out of solution.

Thirteen samples were weighed out in the same manner as for the naphthalene tests and the percentages of distillate added as before. Consistency

¹ Dry.

results were obtained upon the mixture of tar and distillate, according to the float apparatus, and at the same temperatures as in the naphthalene tests—55° C. and 88° C. The procedure was exactly duplicated in both cases, so that the results could be studied under exactly the same conditions. In Fig. 1 the results of this second series of tests are shown by curves B and B', and the corresponding tabulated data are shown in Table I as compared with the results from naphthalene.

The effect exerted by naphthalene upon the fluidity of tar is, from these results, a very important one in coal tars used for road construction. All coal tars contain naphthalene, but the amount in road-tar preparations varies from 0 to 10 per cent. and higher. The degree of fluidity which a tar maintains under service conditions is a most important consideration. The fact that a tar is originally of proper consistency for certain work is no reason for supposing that this consistency will be maintained under service conditions. If the fluidity of the tar is due principally to nonvolatile tar oils, it will undoubtedly maintain its original consistency for a longer period than if the fluidity is due mainly to high naphthalene content. Therefore, in two tars of the same consistency or degree of fluidity, one with a small naphthalene content and the other with a high naphthalene content, it would be natural to predict from the foregoing data that upon exposure the low naphthalene tar would maintain its original consistency for a longer time, if other things were equal. Owing to the volatility of naphthalene, the high naphthalene tar would undoubtedly lose more or less naphthalene, and hence its fluidity might be expected to decrease rapidly. This subject is now under investigation and will be covered in a later paper.

In addition to refined coal tars, refined water-gas tars and also refined mixtures of coal tar and water-gas tar are used to a considerable extent in the treatment and construction of roads. For this reason it was thought advisable to determine what effect naphthalene might have upon the consistency of water-gas tar pitch. Water-gas tar as produced in the modern manufacture of carburetted water gas is similar in many ways to its sister product, coal tar. It has, however, marked characteristics in which it differs from coal tar, namely, a lower specific gravity, a lower free-carbon content, and a relatively small amount of naphthalene.

A representative sample of water-gas tar was distilled until the residual pitch had as nearly as possible the same consistency at 55° C. as the coal tar pitch in the previous experiments. This water-tar pitch had a consistency of 9 minutes and 49 seconds. It was divided into two portions, one for naphthalene mixtures and one for distillate mixtures. As in the previous work, samples were weighed out with varying percentages of naphthalene and a duplicate set of samples with an equivalent amount of the same naphthalene-free tar distillate as used in the coal-tar tests. The consistency was obtained in both sets of tests with the float apparatus, and the water bath

was maintained at 55° C. and 80° C., respectively. The results from the naphthalene series are shown in Fig. 2 by curves C and C', and those of the corresponding distillate series by curves D and D'.

It will be noted that these curves follow very closely those shown in Fig. 1 and are of the same general type. The relation between the consistencies obtained with naphthalene and the naphthalene-free distillate is practically the same as for coal tar, and the respective influence of the increase in fluidity is similar, as shown

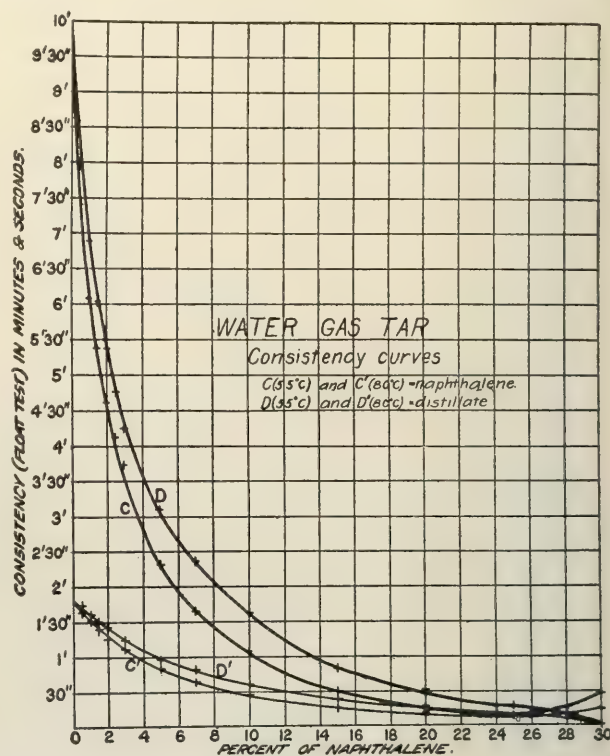


Fig. 2.

in Table III. Indeed, this similarity is remarkably close when it is realized that the coal-tar pitch contained 18.34 per cent. of free carbon, while the water-gas tar pitch contained only 1.77 per cent. of free carbon.

TABLE III.—PERCENTAGE OF INCREASE IN FLUIDITY OF WATER-GAS TAR PITCH, OWING TO ADDITIONS OF NAPHTHALENE AND NAPHTHALENE-FREE TAR DISTILLATE.

Per cent. of naphtha- lene or distillate.	Due to naphthalene.		Due to distillate.	
	At 55° C. Per cent.	At 80° C. Per cent.	At 55° C. Per cent.	At 80° C. Per cent.
0.5	21.1	5.5	18.8	4.6
1.0	38.0	15.6	29.7	11.9
1.5	45.2	22.0	38.5	16.5
2.0	53.0	30.3	45.2	21.1
2.5	57.9	33.0	51.4	26.6
3.0	62.0	38.5	56.7	31.2
5.0	76.4	54.1	68.4	46.8
7.0	83.1	64.2	75.9	55.0
10.0	89.0	75.2	83.5	67.0
15.0	94.9	86.2	91.5	78.9
20.0	97.1	89.9	94.7	86.2
25.0	98.5	92.7	97.1	90.8
30.0	95.2	87.2	100.0	100.0

Comparing these data with those tabulated for the coal-tar tests, it will be noted that the effect

of small percentages of naphthalene is even greater for the water-gas tar than for the coal tar of like consistency, and this is also true of the naphthalene-free distillate, although the effect is not so marked. The principal difference between the two sets of curves at 55° C. is the marked increase in fluidity caused by both naphthalene and distillate when only 0.5 per cent. is added, as even as small an addition as this increases the fluidity by 21.1 and 18.8 per cent., respectively. This fact is shown by the sharp drop in both water-gas tar curves at 55° C. The two series of curves obtained at 80° C. are also similar. The effect of increasing amounts of naphthalene, however, is not so markedly shown as in the curves for the test at 55° C.

In a paper by one of the authors,¹ "On the Effect of Free Carbon in Tars from the Standpoint of Road Treatment" it is shown that an increase in the percentage of free carbon to tar bitumen of a given consistency decreases the fluidity of the resulting product. It is evident, therefore, that the true bitumen of the two tar pitches under investigation, excluding free carbon differed somewhat, although the pitches as prepared were of the same consistency.

While at the present time it does not seem advisable to draw very definite conclusions, the foregoing results nevertheless strongly indicate the following facts:

1. That the fluxing value of naphthalene for tar pitches is somewhat greater, although quite similar, to the heavier naphthalene-free tar distillates, until the mixture becomes saturated with naphthalene.

2. That for the harder tar pitches the addition of very small percentages of naphthalene will produce a marked increase in fluidity of the resulting product.

3. That for the softer pitches the addition of naphthalene in small quantities causes less increase in fluidity than for the harder pitches.

4. That where naphthalene is added beyond the point of saturation a rapid decrease in the fluidity of tars at temperatures below the melting point of naphthalene is observed, but at temperatures above its melting point the fluidity continues to increase.

In conclusion, it may be stated that evidence points to the fact that, within a reasonable degree of accuracy, it should be possible to foretell, by reference to the curves which have been given, what consistency to expect from the addition of a given percentage of naphthalene to a tar pitch or refined tar of known consistency, irrespective of the free carbon content of the tar.

OFFICE OF PUBLIC ROADS,
U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON.

A NEW METHOD FOR DETERMINING THE MELTING POINT OF PITCH.

By H. F. FRENCH.

Received September 25, 1911.

As a criterion for the suitability of coal tar pitch for various industrial purposes, the melting-point

determination has found considerable application. From the nature of the material, such a point is necessarily arbitrary, being fixed only by the conditions imposed in the method selected.

The methods in general use are rendered rather unsatisfactory, by large personal factors, and essential conditions which are very hard to reproduce exactly. This paper describes a new method, designed to remedy these difficulties.

It consists in heating a suspension of the pulverized material in a solution, under definite conditions, until it coagulates. The temperature at which this coagulation occurs is taken as the melting point. The bath is a very dilute solution of sulphuric acid, heated electrically, in itself furnishing the necessary resistance. The electrolyte is rotated in an Erlenmeyer flask. The remainder of the apparatus proper is a unit, consisting of the electrodes and thermometer.

APPARATUS.

Electrodes are $\frac{3}{16}$ -inch copper rod, rubber-covered and lead-tipped, assembled with a 110° Centigrade thermometer, as shown in the figure.

Flask.—An 8-ounce medium mouth Erlenmeyer flask.

Ammeter.—A direct current instrument with at least a 3 ampere scale, graduated in 0.1 ampere divisions.

Electrical Circuit.—A 220-volt direct current circuit.

Electrolyte.—A dilute solution of sulphuric acid.

Preparation: A stock solution is made up containing 20 cc. of concentrated H_2SO_4 , sp. gr. 1.84, per liter. Twenty-five to thirty cc. of this solution are diluted to 1 liter and standardized.

Standardization.—The electrodes are connected to the power circuit, through the ammeter, and a double pole, single throw, knife switch. Fifty cc. of the electrolyte, at about 20° Centigrade, are placed in the flask, and the electrodes introduced. The electrodes should be parallel to one side of the flask with their tips resting upon the bottom. By a few short applications of the current, while rotating the flask, the temperature of the bath is brought to 24° C. At this point the amperage is quickly read. The electrolyte must be of such strength that this reading, which will be obtained at very nearly 25° C., is 2.2 amperes.

Preparation of Material.—About 20 grams of pitch are placed in a one-quart iron mortar, and ground until the bulk of it passes through a screen conforming to the following specifications:

SCREEN SPECIFICATIONS.

Meshes per linear inch.	Number of wire.	Diameter of wire in inches.	Size of openings in inches.
40	32	0.01125	0.0137

The wire number is given according to the Old English Standard Gauge. The screen is made of plain double crimped brass wire cloth.

Determination.—Two grams of the freshly ground material (samples should not be allowed to stand more than one hour after grinding, and should be

¹ *Proc. Am. Soc. Test. Mat.*, 9, 549 (1909).

protected from high temperature) are weighed out within 0.1 of a gram. This sample is transferred to the clean flask, which should be rinsed out with distilled water, and the outside wiped dry.

Fifty cc. of the electrolyte at 20–25° C. are then added, the flask closed with a rubber stopper, and the contents mixed by a slight shaking. The electrodes are now introduced and the flask contents rotated in the same manner as in the standardization, the current is switched on for a moment, and the ammeter reading noted.

A variation of more than one-tenth or two-tenths of an ampere from the initial reading of the electrolyte alone indicates the introduction of some impurity. Such a determination should be started over. If the condition persists, the impurity is probably being introduced in the sample, and should be investigated. If, however, the amperage is very nearly normal, as will be the case with the vast majority of samples, the determination is continued as follows: The flask contents are rotated in the same manner as before, holding the flask at the level of the eyes, and viewing the contents against a good light. The current is now allowed to pass until the pitch coagulates, when the current is immediately switched off, and the temperature quickly read.

It is important to keep the pitch and electrolyte rotating in one direction throughout the determination, and to continue this rotation until the temperature reading has been obtained. It is also essential to the proper performance of the method that the rapidity of this rotation be kept at a maximum.

In noting the end point, a slight, gradual clearing up of the lower part of the solution must be disregarded, and the treatment continued until the large bulk of the material rapidly coagulates into a "gob." Each figure reported should be the average of several determinations.

RANGE AND ACCURACY.

The range of the method is limited by the fact that the samples must be ground as specified, and by the boiling point of the electrolyte. It will be found that these limits allow of the application of the method to practically all samples of what is commonly known as hard pitch. Some experimental work has been done along the line of applying this method to softer varieties of material, by grinding at very low temperatures. These applications, however, have not been worked up extensively, and are, at best, rather inconvenient.

The accuracy of the method is shown by Table 1, which includes all the results obtained during the recent investigation of some special samples. It will be noted that the average figures, obtained by two analysts, who worked independently, agree easily within 1° Centigrade. In addition, this data demonstrates the effect of allowing samples to stand in the ground condition, a point which will receive further mention.

Samples had stood for 15 days in pasteboard containers, after being ground, before the determinations were made.

Variety of pitch.	Sample number.	Analyst A.		Analyst B.		Av. A.		Av. B.	Difference between av. A and B.
		Det.	Det.	Det.	Det.				
		No. 1.	No. 2.	No. 1.	No. 2.				
1	1	70.5	70.5	71.0	71.0	70.5	71.0	0.5	
2	2	75.0	75.0	75.5	75.0	75.0	75.2	0.2	
3	3	83.0	82.0	82.5	83.0	82.5	82.7	0.2	
Freshly ground samples of the same varieties of pitch.									
1	4	65.0	66.0	65.5	..	65.5	65.5	0.0	
2	5	71.5	72.0	71.5	..	71.7	71.5	0.2	
3	6	82.0	82.0	82.5	..	82.0	82.5	0.5	
Same samples (4, 5 and 6) after having stood 10 days in pasteboard containers since being ground.									
1	7	70.5	71.5	71.0	71.5	71.0	71.2	0.2	
2	8	75.0	75.5	75.0	75.5	75.2	75.2	0.0	
3	9	82.5	83.0	83.5	84.0	82.7	83.7	1.0	
Same samples (7, 8 and 9) after having stood in the same conditions for 3 additional days near hot steam pipes.									
1	10	73.0	73.0	72.5	..	73.0	72.5	0.5	
2	11	76.0	77.0	77.5	..	76.5	77.5	1.0	
3	12	84.0	83.0	83.5	..	83.5	83.5	0.0	
Miscellaneous samples.									
		65.0	65.0	66.0	65.5	65.0	65.7	0.7	
		71.5	71.0	72.0	71.5	71.2	71.7	0.5	
		72.0	72.0	71.5	71.0	72.0	71.2	0.8	
		74.0	74.5	74.0	..	74.2	74.0	0.2	
		78.0	77.5	77.0	77.0	77.7	77.0	0.7	
		79.5	79.5	80.0	..	79.5	80.0	0.5	
		82.0	82.0	82.5	82.5	82.0	82.5	0.5	
		86.0	85.5	85.5	86.5	85.7	86.0	0.3	
		86.5	86.0	86.5	..	86.2	86.5	0.3	

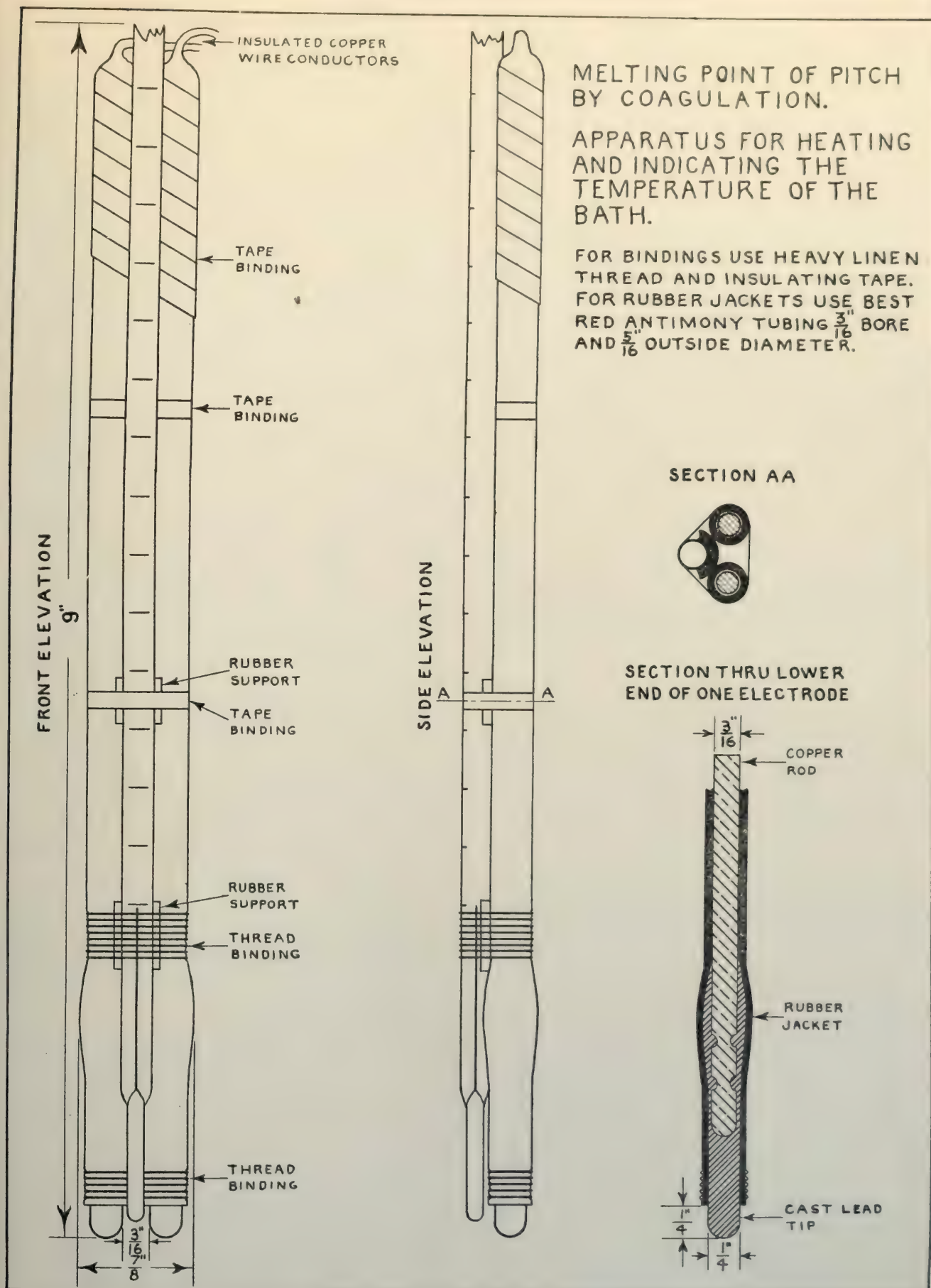
A brief discussion of some additional points may be of interest to any who desire a modification applicable to other materials, and serve to indicate the necessity of the conditions imposed.

HEATING RATE.

Results during the preliminary work led to the conclusion that the heating rate had considerable effect upon the figures obtained. Upon this basis the electrical method of heating was developed, and for some time it was thought necessary to standardize the electrolyte by the rise in temperature over a definite time period of current flow. Subsequent work, however, has disqualified the findings of the earlier experiments, and has shown that the heating rate may be varied considerably without affecting the results to any appreciable extent. Since other methods of heating have not proved nearly so satisfactory as the electrical, this feature has been retained, and the standardization obtained in terms of the amperage, a condition, which, as mentioned below, has considerable effect upon the results.

SHAPE AND SIZE OF APPARATUS.

The apparatus specified has been developed through several more complicated forms. The essential advantage of the one adopted lies in the fact that the rapid rotation throws the bulk of the liquid to the circumference of the flask bottom, thus allowing the electrode tips and thermometer bulb to come into contact with the maximum amount of electrolyte in a given time. This favors a uniform and rapid heat distribution, and a prompt indication of temperature. The same fact permits of the use of a minimum depth of solution, which aids materially toward a rapid end point.



CONDITION OF MATERIAL.

The condition of the ground sample has considerable influence upon the results. Finer material gives lower figures, and in mixtures containing different-sized particles, the finest material present determines the melting point obtained. Since the finest material floats on the liquid, while the coarsest sinks, samples of a mixed nature favor a more uniform distribution of the pitch in the electrolyte. Grinding and sifting tests upon samples of different degrees of hardness, in conjunction with melting-point determinations, demonstrate that the preparation specified furnishes samples with a proportion of fines constantly large enough to regulate this point.

It has also been found that samples, upon standing in the ground condition, yield gradually increasing melting points. Sufficient experimental work has not been done to establish reasons, but the change is probably due to one or both of the following: either a loss of volatile constituents, or a rounding up of the sharp-edged particles by "flowing." These reasons are in some measure indicated by the fact that much greater changes are observed in the softer samples.

AMPERAGE.

Using direct current, the amperage has considerable effect upon the results. With all other factors remaining constant, an increase in amperage raises the melting points obtained. This effect is attributed to the increased amount of gas liberated at the electrodes, and would probably disappear with the use of alternating current.

ELECTROLYTE.

During the investigation several electrolytes have been tried, notably the alkaline hydrates. None of these, however, prove as satisfactory as sulphuric acid, which is particularly adapted to the purpose by its low temperature coefficient.

SIZE OF SAMPLE.

The proper amount of material as given has been selected, with regard to its effect upon the sharpness of the end point, from a series in which this factor was variable.

MISCELLANEOUS CONDITIONS.

The voltage, concentration of electrolyte, size of electrodes, and total size of apparatus may be varied within reasonable limits without appreciably affecting the results. It must be remembered, however, that a change in one of these factors usually involves a variation in some dependent condition which must be kept constant. The necessity of detecting and remedying such a variation is obvious. This procedure, however, frequently involves considerable work; consequently in applying this method to the material for which it was designed, the specifications should be followed absolutely.

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THE COMPOSITION OF TINCTURE OF GINGER.

By HERMANN C. LYTGOE AND LEWIS I. NURENBERG.

Received August 12, 1911.

Some two years ago a sample of powdered Jamaica ginger was obtained and several tinctures were made from it. These were made by the percolation method of the U. S. P., four using the full amount of ginger and alcohol of approximately 95, 70, 50 and 30 per cent. One tincture was made with 95 per cent. alcohol and one-half the specified amount of ginger and another was made with 95 per cent. alcohol, using the ginger previously exhausted with 70 per cent. alcohol. The samples made with 30 and 50 per cent. alcohol were very cloudy and did not settle clear until after standing for several months. After becoming clear, determinations of solids and alcohols were made in these tinctures.

Subsequently some more tinctures were made from Jamaica, African and Cochin ginger, using 95 and 70 per cent. alcohol and also some tinctures were made, from a sample of ginger oleoresin. Two grams of the oleoresin were weighed into each of four 100-cc. flasks and 100, 75, 50 and 25 cc., respectively, of 95 per cent. alcohol were added. The contents of the three latter flasks were diluted with water to the mark, treated with magnesia, and filtered. These samples were then examined by the methods given below and the results are given in Table I. Twenty commercial samples were obtained and examined, the results of which are given in Table II.

Specific gravity was determined with a pycnometer and the index of refraction with an Abbé refractometer.

Alcohol.—Twenty-five cc. were measured into a 100-cc. flask, water was added and, after cooling, made up to the mark, magnesia was added and the mixture filtered. Fifty cc. of the clear filtrate were distilled and after diluting the distillate to 50 cc. its specific gravity and index of refraction (with the immersion refractometer) were determined. The per cent. by volume was multiplied by 4 and from this the per cent. by weight was calculated.

Solids.—Ten grams were weighed into a platinum dish and evaporated on the copper top (not over the live steam) of a water bath, dried at 100° and weighed.

Alcohol-Soluble Solids.—The residue from the total solids determination was dissolved in alcohol according to the method described by Street,¹ filtered, evaporated, dried and weighed.

Water-Soluble Solids.—The residue from the total solids determination was dissolved in water according to the method of Street,¹ filtered, evaporated to dryness and weighed.

Assuming that the terms tincture and extract are synonymous, we have at present two standards for extract of ginger. The U. S. P. standard for tincture of ginger calls for the solution of the alcohol-soluble materials of 200 grams of ginger in 1 liter of the finished product, using 95 per cent. alcohol as the solvent. The standards of purity for food products, Circular 19, U. S. Dept. of Agriculture, require 100

¹ J. P. Street, "Report of Conn. Agricultural Expt. Station, 1910, 516."

cc. of ginger extract to contain the alcohol-soluble material from not less than 20 grams of ginger, no requirement being made as to the strength of the alcohol. It has been the custom to call ginger extract adulterated if made with weak alcohol. Street has shown¹ that extracts made from 60 per cent. alcohol are weaker in alcohol-soluble solids and consequently inferior to those made with 95 per cent. alcohol. Our work, as given in Table I and the plot, shows that in tinctures made from Jamaica ginger if alcohol of 70 per cent. or more is used, the amount of alcohol-soluble material will be about the same in all cases. As the strength of the extracting alcohol is decreased the per cent. of water-soluble solids and total solids increase, and using alcohol below 70 per cent. the alcohol-soluble solids decrease.

As there is undoubtedly some volatile oil present, not determined by these methods, we endeavored to discover and approximately measure it first by the refraction of the distillate and then by means of the Feser lactoscope. It will be noticed in Table I that the difference between the found and calcu-

tinctures made with the weak alcohol. A sample of the tincture made with 95 per cent. alcohol was then distilled undiluted and the specific gravity and re-

Relation between Alcohol and Solids in
Tincture of Jamaica Ginger

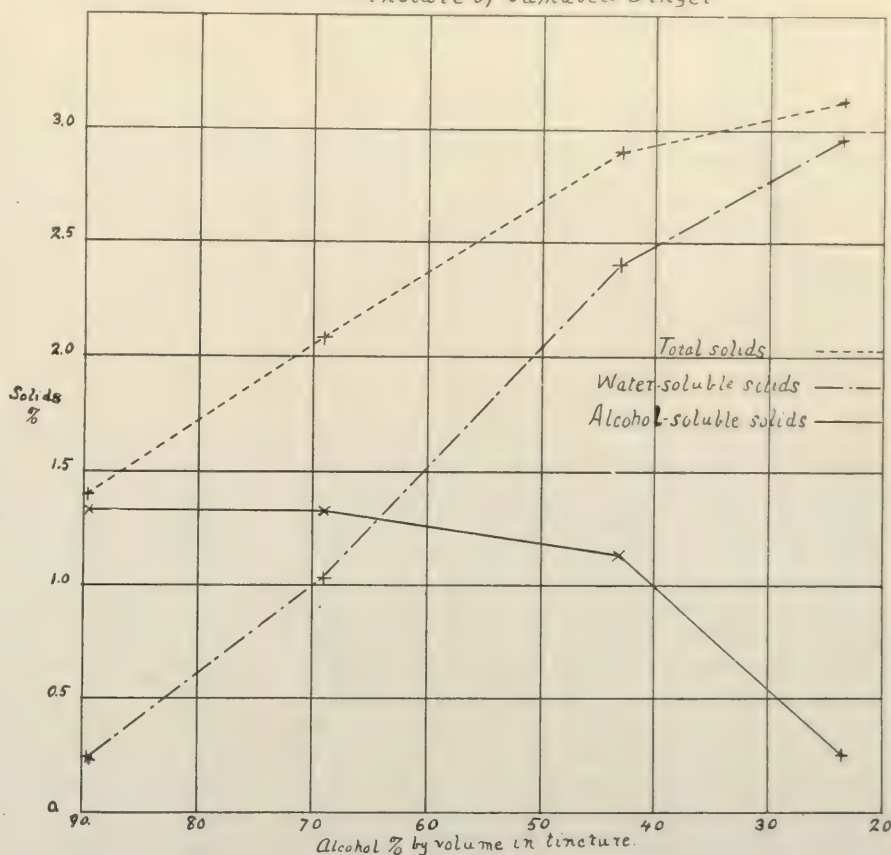


TABLE I.—COMPOSITION OF TINCTURE OF GINGER MADE FROM DIFFERENT VARIETIES OF GINGER AND VARYING STRENGTHS OF ALCOHOL.

Variety of ginger.	Alcohol extract of ginger. Percent.	Cold water extract of ginger. Per cent.	Ginger used per liter. Grams.	Alcohol used. Per cent.	Sp. gr., 20°/4°.	n _D 20°.	Refraction of alcoholic distillate. 20°.		Alcohol.		Solids.			Water used in Feser lactoscope. Amt. of tincture used.	
							Found.	Calc.	By weight. Per cent.	By volume. Per cent.	Total. Per cent.	Alcohol-soluble. Per cent.	Water-soluble. Per cent.	10 cc.	15 cc.
Jamaica.....	5.90	17.30	200	94.53	0.8184	1.3662	47.8	47.5	85.38	89.76	1.40	1.33	0.24	...	60
			200	73.30	0.8863	1.3664	39.2	38.7	61.46	69.08	2.08	1.33	1.04	...	60
			200	49.29	0.9462	1.3609	29.6	29.5	36.66	43.68	2.89	1.13	2.40
Jamaica.....	4.85	17.10	200	29.58	0.9794	1.3518	22.1	22.1	19.13	23.44	3.11	0.30	2.96
			200	95.40	0.8174	1.3658	47.1	46.9	84.70	89.24	1.38	1.10	0.19	...	50
			200	69.34	0.8933	1.3662	37.2	36.9	56.36	64.16	2.22	1.45	1.14	...	70
Jamaica.....	200	95.0	0.8189	1.3657	47.3	46.7	84.19	88.84	1.60	1.24	0.22	...	40
African.....	6.40	12.55	200	95.40	0.8173	1.3665	47.5	46.9	84.84	89.36	1.86	1.84	0.08	105	..
			200	69.34	0.8881	1.3660	37.9	37.7	59.35	66.08	1.90	1.34	0.44	120	..
Cochin.....	6.95	17.00	200	95.40	0.8181	1.3666	47.5	46.9	84.70	89.24	2.19	1.94	0.22	140	..
			200	69.34	0.8889	1.3672	37.0	36.8	55.73	63.56	3.08	1.47	1.86	80	..
Jamaica.....	5.90	17.30	100	94.53	0.8156	1.3645	48.1	47.9	87.82	91.64	0.70	0.67	0.21
Jamaica exhausted with 73.30 per cent. alcohol.....	200	94.53	0.8352	1.3650	46.1	46.1	82.32	87.36	0.18	0.18	0.06
Average of 95 per cent. tinctures.....	200	95.15	0.8180	1.3662	89.29	1.68	1.49	0.19
Average of 70 per cent. tinctures.....	200	69.34	0.8901	1.3665	66.40	2.40	1.15	1.42
Ginger of oleoresin.....	20	95.0	0.8144	1.3668	49.0	47.9	87.24	91.12	1.24	1.16	0.10
			20	75.0	0.8807	1.3658	40.3	38.9	65.06	72.44	1.05	0.86	0.51
			20	50.0	0.9389	1.3593	30.5	29.7	38.23	45.40	1.03	0.50	0.79
			20	25.0	0.9762	1.3484	22.4	21.9	19.33	23.68	0.95	0.18	0.92

lated refractions of the alcoholic distillate in the case of Jamaica ginger tincture made from 95, 70, 50 and 30 per cent. alcohol were 0.3, 0.5, 0.1 and 0, respectively, showing less volatile high refracting substances in the

fraction of the distillate taken, both of which were found to correspond to the same strength alcohol. This is no doubt due to the non-volatility of the essential oil at the temperature of boiling alcohol. Using the Feser lactoscope, 10 cc. of the tincture in

¹ J. P. Street, "Report of Conn. Agricultural Expt. Station, 1910, 505."

TABLE II.—COMPOSITION OF COMMERCIAL TINCTURES OF GINGER.

Sp. gr. 20°/4°.	n _D 20°.	Refraction of alcoholic distillate 20°.		Alcohol.		Solids.			Remarks.	
		Found.	Calc.	By weight. Per cent.	By volume. Per cent.	Total. Per cent.	Alcohol-soluble. Per cent.	Water-soluble. Per cent.		
0.8224	1.3660	46.3	47.8	87.81	91.64	1.23	1.09	0.10	U. S. P.	
0.8173	1.3655	47.2	47.8	84.19	88.84	1.26	1.16	0.19		
0.8221	1.3665	46.6	46.5	83.19	88.04	1.59	1.38	0.27		
0.8229	1.3667	48.0	46.5	72.28	78.92	1.48	1.47	0.24		
Average,	0.8212	1.3663	47.0	47.1	81.85	86.68	1.39	1.28	0.20	
0.8436	1.3688	45.9	44.7	68.68	75.70	2.72	2.36	0.71	Good tinctures but not U. S. P. Low in alcohol.	
0.8491	1.3674	44.8	43.5	66.74	73.67	1.61	1.40	0.57		
0.8555	1.3678	44.3	42.5	65.20	72.57	2.34	2.02	0.49		
0.8985	1.3656	36.4	36.1	54.59	62.44	2.30	1.30	0.84		
0.8959	1.3652	36.6	36.1	54.59	62.44	1.90	1.33	1.23		
Average,	0.8685	1.3670	41.6	40.5	61.95	69.96	2.17	1.68	0.77	
0.9029	1.3642	36.0	35.5	52.58	60.44	1.33	0.95	0.70	Low in alcohol and ginger.	
0.9054	1.3645	36.8	36.0	49.60	54.65	1.42	0.67	1.12	Made from exhausted ginger.	
0.8129	1.3651	48.1	47.5	87.00	91.00	0.88	0.75	0.10	Low in ginger.	
0.8601	1.3659	41.7	40.9	67.60	74.76	0.71	0.66	0.10	Made from oleoresin of ginger and weak alcohol.	
0.9292	1.3596	31.5	30.5	41.62	49.08	0.60	0.18	0.36		
0.9308	1.3651	31.0	30.5	40.58	46.91	0.73	0.46	0.54		
0.9321	1.3596	31.7	31.0	39.00	46.25	0.64	0.56	0.45		
0.9464	1.3563	28.3	27.8	32.93	39.52	0.46	0.33	0.29		
0.9864	1.3394	17.4	17.5	7.75	9.64	0.73	0.16	0.71	Made from oleoresin of ginger, capsicum and very dilute alcohol.	
0.9931	1.3383	16.2	16.2	4.81	6.00	0.98	0.36	0.96		
0.9960	1.3357	15.2	15.6	2.07	2.10	0.43	0.28	0.39		

the case of African and Cochin ginger extracts were placed in the instrument and water added until the marks were visible. In the case of Jamaica ginger, it was necessary to use 15 cc. of the tincture as the turbidity was much weaker. These figures, given in Table I, show that except in the case of Cochin ginger there is but little difference between the extracts made with 70 and 95 per cent. alcohol.

Ginger extracts made from the oleoresin are practically identical with those made from the root when 95 per cent. alcohol is used, but when weak alcohol is used they are vastly inferior, owing to the absence of water-soluble substances. Indeed in some instances, as shown in Table II, they are nothing more than alcoholic beverages or colored water.

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AGING OF FLOUR AND ITS EFFECT ON DIGESTION.¹

By J. A. WESENER AND GEORGE L. TELLER.

Received March 6, 1911.

A great deal of work has been done on the subject of bleached flour with reference to the so-called nitrite and nitrite-reacting material, and how these substances might affect other constituents of the flour, and the use of the flour as an article of food. In a former paper published by us in *THIS JOURNAL*,¹ we gave a full bibliography of the work which had been done up to July, 1909, with the exception of one article by Ladd and Bassett,² which had not come to our notice, and which appeared in the March issue, 1909, of the *Journal of Biological Chemistry*. Since then other experimenters have written on this subject.

In the many digestion experiments which have been made in the effort to throw some light on the influence of flour bleaching upon digestion, the writers appear to have lost sight of the true chemistry which

is involved in the bleaching of flour, and have devoted their energies to investigating the action of enzymes on certain substances which are not present in commercially bleached flour. Furthermore, much of the work that has been done with these substances by certain experimenters is markedly at variance with the results of our own investigations and of some others who have carried out experiments along similar lines.

In addition to the articles which have appeared in print, the consummation of the work done on this subject was brought out in a suit by the United States Government against the Lexington Mill and Elevator Company³ conducted at Kansas City in June, 1910.

Ladd² failed to call attention to our work previously published on this subject. This could not have been an oversight, for our article appeared in the same number of the *American Food Journal* in which one of his own articles was published, and he has in no other place attempted to refute the arguments which we there presented in direct refutation of numerous essential points in articles published by himself.

Attention should be called to two important errors which appear in Ladd and Bassett's² work. On page 76 where they have stated that the nitrogen as nitrite nitrogen in the patent flour which they used was 6.8 parts per million, and in the clear flour 12.95 parts per million, while giving the amount in five grams of the patent flour 0.0034 milligram nitrogen and in the clear flour 2.4159 milligrams of sodium nitrite for 373 grams of the flour. The correct placing of the decimal point would make the amount of nitrite nitrogen in the patent flour 0.68 part per million and in the clear flour 1.29 parts per million of nitrite-reacting nitrogen. These amounts agree closely with what has been conceded to be the average amount of nitrite-reacting nitrogen found in commercially bleached flours. Without entering into detailed criticism, attention should be called to the fact that Ladd has introduced into this article, without new data, conclusions taken from one of his former

¹ Read at the summer meeting of the American Chemical Society, Indianapolis, June, 1911.

publications, and to which we had replied in detail.⁴ For example, references to iodine absorption by the oil of bleached and unbleached flours, and the presence of nitrogen in the oil of bleached and its absence from the oil of unbleached flours.

The digestion experiments on bleached flour as conducted by Ladd and Bassett,² Halliburton,⁵ Mann,⁶ and Hale⁷ have already been criticized by Prof. Rockwood.⁸ The method used by him in his experiments was one which we outlined at the request of the attorneys for the defense in the Kansas City trial, and which was used by their several experts. In addition to the experiments which he has made, we have increased largely the amount of nitrite-reacting nitrogen both by the use of sodium nitrite and by the use of nitrous and nitric acids in bread and flour, and we have also made an effort to guard against the fallacies and errors introduced by the crude methods which were used by several of these experimenters.

The methods used by the several experimenters, including Ladd,² Halliburton,⁵ Mann⁶ and Hale⁷ are open to criticism, in that none of them determined the actual weight of the digested proteid by the nitrogen determination. This we consider the only reliable and absolute method by which to arrive at concordant and positive results. We present below a series of experiments, the purpose of which is to show the actual workings of the different enzymes on the starch, gluten and other proteid substances. The protein digestion was not only determined by ocular measurements, but by actual determination of the nitrogen and the total solids in solution in the digestive fluid.

DIGESTION EXPERIMENTS ON STARCH FROM FLOUR
WHICH HAD BEEN BLEACHED WITH NITROGEN
OXIDES.

For the purpose of obtaining information as to the reliability of Dr. Halliburton's⁵ experiments, in which he claims to have found wide differences in the rate of conversion of starch into sugar by saliva when nitrites in small quantities were present and when they were absent, the following experiments were carried out.

In these experiments were used fresh undiluted saliva, a freshly prepared solution of medicinal pancreatin made by dissolving 0.6 gram of the pancreatin in 100 cc. of water; thin solutions of starch well boiled and diluted with water to make approximately 1.5 grams in 200 cc.; and a solution of sodium nitrite prepared by dissolving 2.1 grams of a good quality of commercial sodium nitrite (more than 99 per cent. pure) in 100 cc. of water. In carrying out the experiments 10 cc. of the starch solution were used, together with 10 cc. of either the saliva or the pancreatin solution and sufficient nitrite solution or its equivalent of water to make a total of 21 cc. These several mixtures were put in a water bath, heated to 40° C. and the digestion allowed to continue until a drop of the liquid brought in contact with a drop of a dilute iodine solution showed no

further blue color, this being substantially the experiment carried out by Halliburton. The results of these experiments are detailed below.

Starch Digestion, Series I.

Cornstarch with pancreatin and sodium nitrite 0, 1 to 1000, 1 to 2000, and 1 to 3200, time till disappearance of blue 14 minutes. Same using saliva, time till disappearance of blue 20 minutes.

Starch Digestion, Series II.

Unbleached flour with nitrites as in Series I. Time of digestion with pancreatin 27 minutes. Time of digestion with saliva 16 minutes.

Starch Digestion, Series III.

Durum flour unbleached containing faint trace nitrite nitrogen and similar durum flour commercially well bleached containing a strong trace of nitrite nitrogen. Time for conversion of each: with pancreatin 22 minutes, and with saliva 17 minutes.

Starch Digestion, Series IV.

Unbleached flour and same after exposure to kitchen for ten days, the former containing no nitrite nitrogen, the latter 3 parts per million. Time for conversion of both by pancreatin 33 minutes and by saliva 29 minutes.

Starch Digestion, Series V.

Cornstarch (alkaline reaction) before and after exposure to air of kitchen for two days and three nights during which exposure the nitrite nitrogen was increased from 0.4 part per million to 3.46 parts. Time for conversion of both by pancreatin 8 minutes.

Starch Digestion, Series VI.

Wheat flour unbleached and bleached by Alsop process 3, 6 and 18 times and containing nitrite nitrogen 0, 2, 5 and 15 parts per million. Time for conversion with pancreatin 20 minutes each.

A possible explanation as to why Halliburton, and perhaps others, was misled in his experiments on starch lies in the fact that some slight excess of iodine is necessary in the presence of protein to produce the blue color with starch. The decomposition of the potassium iodide by nitrites increases the iodine present and produces the blue color where it would be otherwise not apparent because of the deficiency of iodine. Careful experiment along this line has clearly shown this to be true, especially where the larger amounts of nitrite were used.

To get information concerning the reliability of the data obtained by Ladd and also by Halliburton on the digestion of gluten by pepsin, the following experiments were carried out:

Before detailing these experiments attention should be called to the great difficulty of experimenting with material of the nature of raw gluten and also to the fact that raw gluten as it is separated out in the laboratory is never used as an article of food, and that we do not, in the actual consumption of flour, meet with any of the conditions which we get in carrying out the experiments with raw gluten as they were carried out by these two authors.

In carrying out the experiments detailed by Ladd, it was thought best to make an additional series of experiments using a tube containing a perforated disk at the bottom which could be made much more uniform than the tubes containing glass wool which he describes. Tubes used for this purpose were those belonging to the Knorr apparatus for the extraction of fat and consisted of glass tubes about $\frac{3}{4}$ " in diameter, 6" long and with a platinum disk sealed into the tube near the bottom. Tubes were selected in which the perforations in the disks were as nearly uniform as possible. It is hardly to be expected that tubes made in the manner described by Ladd could be uniform, for it would be practically impossible to pack the glass wool so that it should be always the same.

In these experiments as first carried out, ten grams of the flour were washed for gluten and the entire mass of gluten recovered inserted into a tube for each comparative test. The tube was then put in a pepsin digestive fluid prepared substantially as described in the United States Pharmacopeia. The reference given by Ladd to Simon's "Physiological Chemistry" was evidently in error, for in consulting the three editions of this work no description of a solution of this kind was found. He had evidently meant to refer to a book entitled "Manual of Chemistry" by the same author.

The pepsin solution used in these experiments consisted of 500 milligrams of best scale pepsin dissolved in one liter 0.3 per cent. hydrochloric acid solution. Temperature at which the digestion was allowed to take place was practically that of blood heat, being as near 98° F. as possible. A considerable number of these experiments were carried on, all of which led to the same conclusion; namely, that any differences which were apparent in the rate of digestion of the glutes in the several tubes were due to causes other than the presence or absence of nitrites introduced in the flour by the process of bleaching.

The following series may be given as illustrating the results obtained: in this experiment, instead of depending upon the eye to determine when the gluten was sufficiently disintegrated to pass out of the tube, an aliquot part of the liquid was evaporated to dryness and the solids determined. The results given below are the weights in grams of the solids obtained from 10 cc. of liquid withdrawn from each of the bottles in which the digestion was carried on, the same being taken at the end of 21 hours. In this experiment the flour used was the same flour not bleached, bleached 3 times, 6 times, and 18 times by the Alsop process, the amount of nitrite nitrogen being respectively none, 2, 5 and 15 parts per million. The results are given in the following table.

In another experiment carried on to show primarily the great source of error in this method of experimenting, the same flour was taken throughout the entire series, and the glutes obtained by washing the ten grams of flour were treated the same throughout except that in one pair it was tightly folded, in another medium tightly folded, and in a third loosely folded. It will be seen from this table that in those

TABLE I.

Showing amount of gluten disintegrated in tubes as used by Ladd:

	Nitrites in parts per million.	Glass wool tubes. Solids in 10 cc. of digestive fluid.	Fat tubes.
9189.			
Not bleached.....	None	0.102	0.102
3 times bleached.....	2	0.097	0.115
6 times bleached.....	5	0.093	0.096
18 times bleached.....	15	0.118	0.119
9188.			
Not bleached.....	0	0.136	0.127
3 times bleached.....	1.4	0.110	0.106
6 times bleached.....	3.4	0.091	0.130

tubes which contained glass wool there is a wide variation in the amount of solids obtained, due unquestionably to differences in the tubes, although the tubes were made as nearly uniform as possible. The same wide variation is not apparent in the series using the fat tubes.

TABLE II.

Showing variations in results obtained for gluten from same flour, not bleached, when digested as described by Ladd:

	Glass wool tubes. Solids in 10 cc. of digestive fluid.	Fat tubes.
Tight fold.....	0.096	0.133
Medium fold.....	0.057	0.132
Loose fold.....	0.082	0.134

Another series of experiments on the digestion of the raw gluten was carried out substantially as described by Halliburton. 10 grams of moist gluten obtained from the flour used in the experiment tabulated in Table I were introduced into a flask containing 100 cc. of the same pepsin digestive fluid and allowed to digest over night or for about 16 hours. It will be seen from Table III that the results in this experiment are such as to give the greatest apparent digestion for that bleached 3 and 6 times and least for that bleached 18 times, whereas in Table I the greatest digestion was shown for that bleached 18 times. Here again we have strong proof that the variations are due to cause other than the presence of nitrites.

TABLE III.

Gluten digested as described by Halliburton, using ten grams moist gluten in flask containing pepsin solution:

Figures represent grams.	Moist gluten.	Total dry gluten taken.	Gluten not dis- tegrated.	Crude gluten disin- tegrated as deter- mined by evap- oration.	Digested gluten calcu- lated from nitrogen.
Flour 9189.					
Not bleached.....	10	3.34	1.045	2.071	1.616
3 times bleached.....	10	3.26	1.011	2.027	1.632
6 times bleached.....	10	3.48	1.118	2.336	1.942
18 times bleached....	10	3.49	1.513	1.90	1.510

Still further proof of the fallacy of the results of Halliburton's and Ladd's experiments on the digestion of gluten is apparent from experiments on bread in which nitrites were absent as compared with other experiments in which they were present in considerable quantities. These experiments may be divided into four series.

In the first series bread from the same unbleached

flour was made in the usual manner and also by introducing into the water used in making the dough a quantity of the mixed nitrous and nitric acid produced by the solution of nitrogen oxides in water. In the second series the same bread was treated with pepsin hydrochloric acid liquid with and without the addition of varying quantities of sodium nitrite. In the third series flour was used in place of bread as in experiment 2, while in the fourth series the same bread was used throughout the experiment and the hydrochloric acid was replaced wholly or in part by nitrogen acids produced by dissolving nitrogen oxides in water. In all of these experiments the results agree in showing that unless exceedingly large quantities of nitrites are present there is no retardation of the process of digestion.

BREAD DIGESTION EXPERIMENT NO. 1.

Two loaves of bread were made from Pillsbury's Best flour, not bleached, using 350 grams flour for each. One was made according to our regular formula; the other made in an exactly similar manner, except that in making the dough a part of the water was replaced by sufficient acid, prepared as described below, to equal 10 cc. of decinormal alkali. The acid was prepared by passing into water nitrogen oxides produced by diluting well with air the gases given off by acting on ferrous sulphate by nitric acid. The amount of nitrous acid present in this liquid was determined both by use of potassium permanganate and colorimetrically, and it was found that of the acid present in the 10 cc. of decinormal acid used 7.6 cc. were to be attributed to nitrous acid and 2.4 cc. to nitric acid. The two loaves of bread produced did not differ materially in any particular except that the one containing the acid was a trifle larger and of better form, just as we have often found by adding a small amount of other acids to bread. It is worthy of note that the bread from the loaf containing the acid was not more bleached than the other, showing that the bleaching gases act on the coloring matter of the flour only when the flour is in its dry condition. The acidity of the two loaves of bread was determined and, expressed as lactic acid, was 0.22 per cent for the loaf without the acid, and 0.20 per cent. for the loaf with the acid. The nitrite nitrogen in the bread without acid was 0.03 part per million, and that from the one containing the acid was 0.2 part per million. The nitrite nitrogen added to the loaf containing the acid was 30 parts per million calculated on the flour. The original flour contained traces of nitrites taken up from the air.

On the morning after the bread was baked portions of the interior of each loaf were grated as uniformly as possible. The crust was rejected to permit of greater uniformity of sample. 20 grams of each bread were introduced into a bottle and to each was added 200 cc. of a solution of pepsin and acid, containing 0.100 gram of pepsin and sufficient hydrochloric acid to make 0.3 per cent. To another two bottles were added 20 grams of each bread and 200

cc. of a pancreatin solution containing 0.112 gram pancreatin and 0.6 gram sodium bicarbonate. Also two other bottles containing bread and water only. All were kept at a temperature of 38° C. for one hour after which they were filtered and 25 cc. of each filtrate taken in duplicate for the determination of nitrogen by the Kjeldahl method. The results obtained were as follows, after correcting for the pepsin and pancreatin added and expressed as protein in per cent. of bread taken:

	Plain loaf. Per cent.	Acid loaf. Per cent.
Water only.....	0.54	0.54
Pepsin digestion.....	6.34	7.45
Pancreatin digestion.....	4.00	3.71

BREAD DIGESTION EXPERIMENT NO. 2.

In further study of the effect of nitrite nitrogen on the digestive ferments, bread was baked from Pillsbury's Best flour (not bleached) according to our usual formula and also by substituting for a part of the water, water containing an amount of hydrochloric acid equivalent to ten cubic centimeters of decinormal acid together with an exactly equivalent quantity of sodium nitrite, and to a third loaf hydrochloric acid equivalent to 20 cc. of decinormal acid together with its equivalent of sodium nitrite.

The three loaves of bread were substantially the same in appearance, except that one containing the greater amount of nitrite was somewhat darker and both those containing acid were slightly larger than that containing no acid. The acidity of the bread as baked was determined and found to be 0.13 per cent. for the loaf containing no acid, 0.12 per cent. for each of the other two calculated as lactic acid; and the amount of nitrite nitrogen in the bread was found to be a trace for that to which no nitrite was added and 3.0 parts per million for each of the other two. The digestion was carried out as in bread experiment No. 1 except that 0.020 gram of pepsin was used to each 20 grams of bread. In the table given the loaves are designated by the actual amount of nitrite nitrogen added to the bread as calculated upon the flour used, which in the case of the 10 cc. acid loaf was 40 parts per million and for the 20 cc. loaf 80 parts per million.

The amount of protein extracted from the bread is calculated in per cent. of the moist bread taken for digestion.

	Plain loaf.	40 parts ni- trite loaf.	80 parts ni- trite loaf.
Water extract.....	0.52	0.44	0.49
Pepsin extract.....	6.0	5.40	6.06
Pancreatin extract.....	3.9	4.0	4.60

BREAD DIGESTION EXPERIMENT NO. 3.

This experiment was made exactly similar to experiment No. 2. Four loaves were made: one without acid and nitrite, the others with hydrochloric acid and nitrite equivalent to twenty, thirty and forty cubic centimeters of decinormal acid respectively, and containing nitrite nitrogen expressed in parts per million of the flour as follows: 80, 120, 160. The loaf containing the greater amount of nitrite was

somewhat smaller than the other three, much darker in color when cut, and had a peculiar unpleasant odor. The other two loaves were also perceptibly darker than that without nitrite. The determined acidity of all loaves was the same, 0.12 per cent. expressed as lactic acid for the moist bread. The nitrite nitrogen present expressed as parts per million of the moist bread was as follows: trace, 2, 5 and 12 parts per million. All the breads contained substantially the same amount of moisture. The protein obtained from the bread by the water, pepsin and pancreatin liquids was as follows:

	Water.	Pepsin.	Pancreatin.
Loaf with no nitrites.....	0.72	4.50	3.64
Loaf with 80 parts per million.....	1.00	5.20	4.16
Loaf with 120 parts per million.....	1.20	4.80	4.16
Loaf with 160 parts per million.....	1.12	4.52	4.04

Each of these four breads after being grated were put in fruit jars and on the fifth day after baking all had many small colonies of mold started in various parts of the mass, the condition for each bread whether containing nitrites or none being substantially the same.

The solids in solution after the digestion in bread digestion experiments Nos. 2 and 3 were determined by evaporating 10 cc. of each solution to dryness in a weighed porcelain dish. The weights of the residue for the 10 cc. are given in table below:

Experiment No. 2. Added nitrites:	Water.	Pepsin.	Pancreatin.
No nitrites.....	0.066	0.136	0.460
40 parts nitrite nitrogen.....	0.073	0.133	0.471
80 parts nitrite nitrogen.....	0.075	0.142	0.495
Experiment No. 3. Added nitrites:			
No nitrites.....	0.062	0.100	0.297
80 parts nitrite nitrogen.....	0.067	0.131	0.142
120 parts nitrite nitrogen.....	0.072	0.110	0.137
160 parts nitrite nitrogen.....	0.085	0.120	0.230

The somewhat remarkable results with the pancreatin in experiment No. 3 were verified by a second trial with results almost identical with the first.

BREAD DIGESTION EXPERIMENT NO. 4.

Bread showing faint trace of nitrites was grated and divided into 20-gram lots for digestion as in other experiments. 200 cubic centimeters of 0.3 per cent. HCl and 20 milligrams pepsin were used with and without sodium nitrite. A test with plain water and pepsin, water only, and hydrochloric acid only was carried on at the same time. The amount of sodium nitrite used was 0.001, 0.010, 0.050 and 0.100 gram equivalent to 10, 100, 500 and 1000 parts per million nitrite nitrogen calculated on the bread. The protein in solution expressed in per cent. of bread and calculated from the nitrogen determined was as follows:

	Per cent.
Water and bread only.....	0.64
Hydrochloric acid and bread only.....	0.80
Bread, pepsin and water.....	0.8
Bread, pepsin, hydrochloric acid.....	5.66
Bread, pepsin, hydrochloric acid and 0.001 gram sodium nitrite.....	5.38
Bread, pepsin, hydrochloric acid and 0.010 gram sodium nitrite.....	5.79
Bread, pepsin, hydrochloric acid and 0.050 gram sodium nitrite.....	5.18
Bread, pepsin, hydrochloric acid and 0.100 gram sodium nitrite.....	4.51

BREAD DIGESTION EXPERIMENT NO. 5.

A sample of bread bought in the open market and

which contained only a trace of nitrite nitrogen was grated as in other trials and weighed into lots of 20 grams each, and digestion experiments with pepsin were made in duplicate using 100 mg. pepsin and 200 cubic centimeters of liquid to each lot. One lot contained pepsin, water and bread only. Another contained hydrochloric acid equivalent to 0.15 per cent. of the liquid used; and in three others this equivalent of hydrochloric acid was replaced entirely, one-half replaced and one-fourth replaced by dissolving in water nitrogen peroxide produced by blowing air freely through the gases resulting from the action of nitrous acid on ferrous sulphate.

The total acidity of this liquid was equal to 42.5 cubic centimeters decinormal alkali for 100 cubic centimeters, and 100 cubic centimeters required 32.0 cubic centimeters decinormal potassium permanganate to oxidize it. This shows the presence of 16 cc. of decinormal nitrous acid in each 100 cc. and by difference we find 26.5 cc. of decinormal nitric acid present. 200 cc. of the acid solution contained an equivalent of 32 cc. decinormal nitrous acid containing 0.0448 gram nitrite nitrogen which, calculated to the twenty grams of bread used, was equivalent to 2240 parts nitrite nitrogen per million. In those tests in which the one-half and the one-fourth quantities nitrogen acids were used there were present 1120 and 560 parts per million nitrite nitrogen acid calculated on the bread.

The digestion of all the samples of bread was allowed to continue at 38° C. for one hour, at the end of which time all were allowed to filter for one hour, when 10 cubic centimeters of each solution were taken for determination of nitrogen. At the end of one-half hour's time it was evident from the appearance of the bread that all of those in which acid was present were digesting rapidly. No difference in appearance could be detected except that the contents of those flasks containing all nitrogen acids were of a pale lemon-yellow color. Those containing one-half nitrogen acids were distinctly less yellow, those containing one-fourth nitrogen acid were only slightly colored, and those containing only hydrochloric acid were uncolored. The filtered liquid from all these four lots gave well marked biuret reaction.

The average amounts of protein in solution as determined from the nitrogen and calculated as per cent. of bread were as follows:

	Digested protein. Per cent.
Water, pepsin and bread.....	1.36
Nitrogen acids, pepsin and bread.....	7.44
1/2 nitrogen acids, pepsin and bread.....	8.36
3/4 nitrogen acids, pepsin and bread.....	9.00
Hydrochloric acid, pepsin and bread.....	8.75

FLOUR DIGESTION EXPERIMENT NO. 1.

This experiment is similar in all particulars to bread digestion experiment No. 4, except that 20 grams of flour, unbleached and containing no nitrite, were used in place of bread. The results obtained

are calculated as protein ($N \times 5.7$) in per cent. of the flour used.

	Per cent.
Flour and acid only.....	7.94
Flour, water and pepsin.....	2.69
Flour, acid and pepsin.....	11.13
Flour, acid, pepsin and 0.001 gram sodium nitrite.....	11.00
Flour, acid, pepsin and 0.010 gram sodium nitrite.....	10.72
Flour, acid, pepsin and 0.050 gram sodium nitrite.....	11.13
Flour, acid, pepsin and 0.100 gram sodium nitrite.....	10.94

FLOUR DIGESTION EXPERIMENT NO. 2.

In this experiment the same flour not bleached, bleached by Alsop process 3 times, 6 times and 18 times, and strongly bleached by nitrosyl chloride was treated by digestive fluids just as was the bread in bread digestion experiment No. 2. 20 grams of the flour were used, and the amounts of nitrite nitrogen present were 0, 2, 5, 15 and 0.3 parts per million. The results show digested gluten in per cent. of protein on the flour and also the total solids in solution as found by evaporation, and calculated as per cent. of flour.

PEPSIN DIGESTION.

	Solids in solution.	Protein in solution.
Not bleached.....	15.26	9.66
3 times bleached.....	15.42	9.98
6 times bleached.....	15.96	9.75
18 times bleached.....	16.25	9.63
Nitrosyl chloride bleached.....	15.89	9.66

PANCREATIN DIGESTION.

Not bleached.....	20.78	9.34
3 times bleached.....	19.96	8.70
6 times bleached.....	21.28	9.70
18 times bleached.....	20.06	9.47
Nitrosyl chlorid bleached.....	21.28	9.12

FIBRIN EXPERIMENTS.

Halliburton made use of Grutznier's method of comparing digestibility to show that nitrites inhibited the digestibility of fibrin by pepsin. This method depends upon the color imparted to the digestive fluid by digesting fibrin which has been stained with carmine. That this method does not furnish reliable data in the presence of nitrites is apparent from the following:

Fibrin was obtained from ox blood by heating the coagulated blood in salt water until the blood coloring matter had entirely disappeared. This finely divided fibrin was then stained with cochineal (carmine) dried between blotters and weighed.

A series of three experiments was run, each containing 0.6 gram fibrin and 10 cc. of digestive fluid (0.06 gram pepsin in 100 cc. 0.2 per cent. HCl). To one was added 2 cc. of water, to another 1 cc. NaNO_2 solution (0.125 gram in 100 cc.) and 1 cc. of water, containing therefore nitrite nitrogen equivalent to 20 parts per million. To the third was added 2 cc. of the sodium nitrite solution equivalent to 40 parts nitrite nitrogen per million. After $5\frac{1}{2}$ hours the same amount was found digested in each (a very small residue being left) but the color in those containing NaNO_2 had become orange or almost yellow, while the one without nitrite was a deep crimson. In water solution alone it was found that nitrites quickly destroyed the color of carmine. A small

amount of nitrite added to a part of the digested solution in the blank soon changed the color from red to yellow. This error of Prof. Halliburton⁵ was pointed out by us to the several experts in the Kansas City trial, including Prof. Rockwood,⁶ at the time that we sent them our method of making these digestive tests early in 1910.

In these experiments the digestion was allowed to continue for 17 hours as in the experiments made by Halliburton. At the end of this time all solutions were filtered and equal portions of each filtrate taken for estimation of digested fibrin from nitrogen determined by the Kjeldahl method. The results were as follows, expressed in grams of fibrin in solution:

Amount of nitrite.	Fibrin digested. Gram.
None.....	0.184
20 parts nitrite nitrogen per million.....	0.189
40 parts nitrite nitrogen per million.....	0.189

While recognizing the fallacy of the above several experiments as to their bearing upon the bleached flour controversy because of the use of sodium nitrite, nitrous and nitric acids (which do not exist in commercially bleached flour) we have carried on these experiments to show the errors in the work and conclusions of Ladd,² Halliburton,⁵ Mann⁶ and Hale.⁷ It naturally will be seen that the animal experiments conducted by Hale⁷ wherein he used large quantities of sodium nitrite, nitrous and nitric acid, both internally and by subcutaneous injection, have no bearing upon the question as to what the deleterious effect might be of the so-called nitrite-reacting material in flour. The samples of flour which he treated in his laboratory did not represent the commercial operation of bleaching flour, and we know from experiments that we have conducted along this line that flour treated with oxides of nitrogen to the extent as given by this experimenter would be wholly unfit for commercial purposes and would not pass even the ordinary crude flour inspection. We have for a long time recognized that an entirely different substance is produced in bleached flour during the process of bleaching by nitrogen oxides and similar substances.

It is not our purpose at this time to go into the detailed experiments which we have made on this phase of the subject, but only to call attention to some of the more important facts bearing on the chemistry of decolorizing the natural color of flour.

In a previous article,¹ we called attention to the fact that the coloring matter of flour is of the same nature if not identical with carotin, and we have carried on a large number of experiments upon these coloring matters to determine their character. We have satisfied ourselves that they are practically identical in all particulars and are chemically associated with a large class of colors widely distributed in nature, among which may be mentioned the coloring matter of pumpkins, palm oil, June butter, and naturally the grasses from which June butter is produced. We have in various ways made compounds of this coloring matter with nitrogen oxides, nitrosyl

chloride and similar agents, and have again recovered not only the mineral agents with which the coloring matter was treated, but in some cases the coloring matter itself.

This property of uniting directly with nitrogen oxide, nitrosyl chloride, etc., is a well-known characteristic of terpenes. We have found, too, that the compounds formed with oxides of nitrogen and certain terpenes respond to the Griess reagent, just as does the compound formed by the coloring matter of flour with oxides of nitrogen and nitrosyl chloride. In both cases the reaction in the development of the characteristic pink produced by the Griess reagent develops more slowly than when an equivalent amount of inorganic nitrite or nitrous acid is used. We might also mention in this connection that certain nitroso bodies, such as nitroso phenol, also respond to the Griess reagents for nitrites. These reactions indicate that the Griess reagent will take up the NO group from these compounds and react with it in the same manner as though it were a nitrite.

The coloring matters above mentioned, whether distributed as they are in food products, or in a suitable solvent such as chloroform, or in the pure crystalline condition, take up nitrogen oxides with great avidity, being in this nature akin to basic substances. We have found that the nitrogen oxides which are always present in the air combine with this coloring matter much as they do with the alkaline residue which remains in alkali starches, and that such starches when exposed to the air take up appreciable quantities of nitrite nitrogen and respond to the Griess reagent. When flour is exposed to ordinary air it takes up readily the nitrogen oxides and becomes bleached just as it does when exposed to the gases of the electric bleaching machine. Evidently the artificial aging of flour is identical with the natural aging which has been going on ever since white flour was produced. This explains why flour in well ventilated warehouses and bakers' storehouses age more rapidly than when stored under other conditions. Flour which we have exposed to the outside air and to the air of living rooms we have found aged very rapidly. When exposed in the kitchen the yellow color will disappear within 24 to 48 hours, and the extent of nitrite nitrogen taken up may be in excess of the average one part per million which is found in flours which have been bleached by the electrical process.

In one experiment which was conducted, we have found as high as four parts per million nitrite nitrogen in flour thus bleached. A sample of alkali cornstarch, which was packed in a carton and sealed with a paper wrapper, took up nitrite-reacting nitrogen to the extent of 3.85 parts per million after standing for about five weeks in a well ventilated living room. We have even found that bread from unbleached flour exposed to the air of a kitchen over night contained more nitrite nitrogen in the morning than did fresh bread baked in the same manner from a flour which had been artificially bleached with nitrogen oxides.

It is our purpose in a future article to give the

results of these experiments in detail, and to show the actual composition of the coloring matter itself. This much is given as being essential to the line of thought which we wish to bring out in our present article.

Having shown the nature of the compound in bleached flour, and that it responds to the nitrite reaction with the Griess reagent, and as no experimenter up to this time has proved the presence in commercially bleached flour either of sodium nitrite, nitrous or nitric acids, we feel justified in believing that the so-called nitrite reaction in bleached flour is due to this compound. The purified coloring matter of flour combines with comparatively large amounts of oxides of nitrogen and nitrosyl chloride, as we have repeatedly demonstrated in our experiments on weighed quantities of the coloring matter. We have further proved in trials where bleaching was being practiced on a commercial scale that in nearly all instances one pound of liquefied nitrosyl chloride gas will bleach 1000 barrels of flour, and often as high as 2000 barrels. Knowing then the chemistry of bleaching flour, it will be recognized at once that if there is any toxic substance in the flour it must be due to this substance, and any and all animal experiments which have been conducted by the several experimenters using sodium nitrite, nitrous or nitric acids from whatever source obtained, have no bearing whatever on the true chemistry of bleaching nor upon the toxic effect which the substance developed may have upon animals. Extensive experiments which we, Haines,⁹ Wilcox and Luff,¹⁰ Hale,¹¹ and others have conducted in feeding bread and extracts from commercially bleached flour have failed to show any indication of a toxic or pathologic effect upon animals consuming the same. Further than this Vaughan¹² has experimented with the coloring matter containing the NO group which is produced in the bleaching of flour. He took 2 pounds of unbleached flour and extracted this with 2 liters of petroleum ether. The ether was separated by filtering and then through this was passed a current of oxides of nitrogen prepared by the action of nitric acid on copper. The coloring matter held in solution was bleached and precipitated. The precipitate was collected and washed with petroleum ether. Practically the whole of this precipitate was introduced into the stomach of a rabbit which had been kept fasting for two days. This had no recognizable effect on the rabbit, nor did it alter the spectroscopic appearance of its blood. The substance gave Liebermann's nitroso test.

CONCLUSIONS.

Nitrites do not interfere with diastase in its action on starch, even when present as sodium nitrite to the extent of one part in 1000.

Nitrous and nitric acid do not inhibit the action of peptic digestion, and may wholly replace hydrochloric acid in this essential first stage of digestion, while digestion by pepsin without acids will not take place.

While pancreatic digestion will not take place in

the presence of free acids, it is not inhibited by the presence of relatively large quantities of nitrites, nor is its action restrained on the proteid which has been previously subjected to appreciable quantities of nitrous and nitric acids.

No experiments by the several writers on this subject have demonstrated the presence in commercially bleached flour of either mineral nitrite, nitrous or nitric acids.

The nitrite-reacting material of flour, as far as we have been able to determine, is entirely due to the direct union of the coloring matter and the nitrogen oxide.

Vaughan has shown that the substance which gives the nitrite-reacting material and which responds to Liebermann's nitroso reaction is not poisonous nor does it have any action on the blood.

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SOME OBSERVATIONS UPON THE ASSAY OF DIGESTIVE FERMENTS.

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The digestive ferments have many characteristics peculiar, for the most part, solely to themselves.

PEPSIN.

These various characteristics are well illustrated by the enzyme pepsin, and to explain I wish to present the following experiment. As is well known the U. S. P. test for pepsin reads as follows: "Im-

merse a hen's egg, which should be *fresh*, etc." Certainly this wording seems sufficiently simple, plain and explicit, but in reality it becomes evident to any one conducting a long series of tests, that the words "fresh eggs" are decidedly loose and inaccurate.

The "fresh egg" of the housekeeper and epicure may successfully pass the test of a sensitive palate and yet prove unsuited for the purpose here.

This then halts us at the beginning of our experiment to ask "what constitutes a fresh egg, and do all fresh eggs give concordant results?"

To answer this question I collected 21 eggs from a number of chickens. The eggs had all been laid on the same day and the chickens all belonged to one man and had been kept under the same conditions for months. With these eggs, I tested two samples of pepsin, one marked 1 : 3000 and the other 1 : 10,000, starting the test on the second day after the eggs had been laid and continuing every following day up to and including the 10th, with the following results.

The tests clearly demonstrate the fact that an egg may be fresh and give an assay which varies from one to two thousand units. One chemist working with eggs two days old would assign a digestive activity to a sample of pepsin from one to two thousand units lower than another chemist working under exactly similar conditions, but using eggs which were five to six days old. I should, therefore, like to suggest that when chemists are assaying pepsin that they satisfy themselves as to the age of the eggs which they are using before proceeding with the test. Eggs, however, do not always give the highest result between the 5th and 7th day, but it is safe to say that on an average, eggs which are between 5 to 7 days old give the maximum activity to a sample of pepsin.

The effect of the age of the egg is particularly noticeable in the case of the 1 : 10,000 pepsin where the residue on the 2nd day eggs was 3 cc. and on the 5th day had decreased to $\frac{9}{10}$ of one cc., and after the 5th day the residue started to increase until on the 10th day it was the same as on the 2nd day.

The above experiment illustrates how sensitive the pepsin is to the nature of the albuminoid upon which it is acting.

To show how reactive it is to environment it is interesting to note that the activity of pepsin is not only inhibited in neutral solution, but in proceeding to the alkaline reaction the pepsin is soon destroyed, and even in an acid menstruum in which the pepsin normally is most active, a difference of 0.025 per cent.

Laid on 31st. Sample No.	Strength tested for.	April 3rd. 2 days.		April 4th. 3 days.		April 5th. 4 days.		April 6th. 5 days.		April 7th. 6 days.		April 8th. 7 days.	
		Residue.	Strength.	Residue.	Strength.	Residue.	Strength.	Residue.	Strength.	Residue.	Strength.	Residue.	Strength.
Number 1 1 :	3,000	0.8 cc.	—	0.5 cc.	—	0.3 cc.	—	0.3 cc.	—	0.4 cc.	—	0.6 cc.	—
Number 1 1 :	3,250	1.0 cc.	1 : 3,250	0.6 cc.	—	0.4 cc.	—	0.4 cc.	—	—	—	—	—
Number 1 1 :	3,500	1 $\frac{1}{4}$ cc.	—	0.9 cc.	1 : 3,500	0.7 cc.	1 : 3,500+	0.6 cc.	1 : 4,000	0.6 cc.	—	1.0 cc.	1 : 3,500
Number 1 1 :	4,000	—	—	—	—	—	—	—	—	1.0 cc.	1 : 4,000	1 $\frac{1}{2}$ cc.	—
Number 2 1 :	10,000	3.0 cc.	—	2 $\frac{1}{2}$ cc.	—	1 $\frac{1}{2}$ cc.	9,000	$\frac{9}{10}$ cc.	1 : 10,000	$\frac{9}{10}$ cc.	1 : 10,000	2 cc. +	—
Number 2 1 :	8,000	2 $\frac{1}{2}$ cc.	7000	1 $\frac{1}{2}$ cc.	7000+	$\frac{7}{10}$ cc.	—	$\frac{4}{10}$ cc.	—	$\frac{9}{10}$ cc.	—	1 cc.	8,000
Number 2 1 :	6,000	$\frac{9}{10}$ cc.	—	$\frac{9}{10}$ cc.	—	$\frac{5}{10}$ cc.	—	$\frac{3}{10}$ cc.	—	$\frac{3}{10}$ cc.	—	$\frac{4}{10}$ cc.	—

acid more or less than 0.309 per cent. shows a variation in the amount of albumen digested, and 0.05 per cent. more or less acid will show a difference of 3 cc. in the residue.

Some chemists who have observed the variations in the assay of this enzyme have sought a remedy in the use of dried egg albumen, but if the albumen in the moist stage gives such wide variations when used for assay, the dried albumen must of necessity do the same. I should, therefore, recommend that each individual adopt a standard pepsin which has been assayed by eggs of different age, and then check all future samples against said standard.

PANCREATIN.

Another enzyme showing the same peculiar characteristics as pepsin is pancreatin.

Pancreatin is a combination of trypsin, amyllopsin and steapsin, together with myopsin and more or less extraneous matter.

The Pharmacopoeia gives two assays for this preparation, one of which measures its proteolytic or tryptic strength and the other its amylolytic or starch hydrolyzing power. The milk or trypsin test has not proven satisfactory in my hands and I consider the test too rigid. The difficulty seems to be in what is meant by the wording "some nitric acid," also as of what a "coagulation" consists, and where coagulation ceases and separation and precipitation commence. Inasmuch as pancreatin, if taken internally, is used for its starch hydrolyzing power, and its tryptic enzyme would be killed in passing through the stomach, most manufacturers to-day do not apply the milk test at all. The tryptic strength can be of value only in the preparation of pre-digested foods.

The other assay which measures the amylolytic strength gives very satisfactory and concordant results, but amyllopsin, and in fact, all diastatic enzymes do not react the same upon all kinds of starch. Although cornstarch is official, it is interesting to note that many manufacturers use potato starch in assaying diastatic ferments, and a great variation exists in the strength of a diastase when stated in terms of potato starch or cornstarch. To be brief, I should say that pancreatic diastase shows $\frac{1}{3}$ more activity when tested upon potato starch than when tested upon cornstarch, or to state it in another way—a pancreatin which tests 1 : 50 in 10 minutes on potato starch would require 15 minutes when tested upon cornstarch under identical conditions. The great variation in gauging the color of the digested starch solution when added to the iodine can be prevented by all chemists checking the digestion until 4 drops of the digested starch solution cease to give any color whatever when added to the iodine solution.

A third test for pancreatin which is not official, but which I have used with good success, measures the strength of the steapsin or the fat-splitting enzyme present. The test is as follows:

Weigh out 5 grams of a 50 per cent. emulsion of almond oil into a small Erlenmeyer flask, add 25 cc. of a solution of sodium bicarbonate (20 grams to

8 ounces) (1 gram to 182 cc.). Mix thoroughly, place the flask in a water bath at 40° C. and let stand until the mixture is exactly 40° C., then add 0.1 gram ferment. Mix a second time, replace in the water bath and maintain at 40° C. for $\frac{1}{2}$ hour, gently inverting the flask every 5 minutes. At the end of 30 minutes' digestion, remove the flask from the water bath, transfer the contents to a beaker, heat to boiling and titrate the alkalinity with $N/10$ H_2SO_4 using phenolphthalein as an indicator. Run a blank at the same time. The difference between the alkalinity of the blank and the alkalinity of the sample to which the ferment was added represents the sodium bicarbonate neutralized by the free fatty acid liberated by the action of the steapsin.

RENNET.

The third important animal enzyme showing the peculiarities of these digestive ferments is rennet and the standard rennet on the market to-day is what is labeled as 1 : 30,000, which means that, assuming a standard milk gallon as weighing 60,000 grains, one grain of rennin will curdle $\frac{1}{2}$ gallon of milk (or 30,000 grains) in 10 to 12 minutes. This enzyme shows its selective characteristics as to the nature of proteid, temperature and reaction of media, and results sometimes vary when different samples of milk are used from different cows, but I have found that with the following method of procedure very concordant results are obtained.

In selecting the milk to be used I stipulate fresh milk and request that it has not been pasteurized or heated in any way. Two quarts of this milk are heated to 40° C. and to this is added 10 cc. of a solution of rennin containing 0.4843 gram in 150 cc. water. I never stir the milk, but mix the rennin by pouring from one receptacle to another. The time of mixing is noted and at $\frac{1}{2}$ -minute intervals thereafter the milk is gently tipped to one side. By this means coagulation can be detected the moment it commences, and at the congealing point the milk should separate into a solid casein mass and liquid whey. I find that the best commercial samples congeal in 10 to 12 minutes.

PAPAIN AND BROMELIN.

As in the animal kingdom we have juices whose specific function is to tear asunder the food material to make it available for the needs of the body, so in the plant kingdom we find analogous enzymes whose function is exactly the same, that is, to render the plant's food assimilable.

Most important among these enzymes which man has appropriated to his use are bromelin and papain. Bromelin occurs in the juice of the pineapple, and papain the fruit of the paw-paw, a tree growing in the tropical countries of the Bahamas and the West Indies.

The paw-paw tree attains its full bearing capacity in a year. It produces from 40 to 50 paw-paws of a dark green color, ripening to a deep yellow. The shape and general appearance of the paw-paw fruit is very similar to a squash. In collecting the papain

a very light superficial incision, not over $\frac{1}{8}$ of an inch in depth, is made in the fruit from which exudes a clear water-like juice, which on exposure to air becomes opaque. The milky fluid will run for a short time, but soon coagulates; when this takes place the coagulated juice is brushed off and a fresh incision made, thus producing another but smaller yield of juice. The scorings are thus made about $\frac{1}{2}$ inch apart all around the fruit and the tappings are usually made just previous to ripening.

The juice must be collected in porcelain-lined receptacles as it is very corrosive and would not only injure metal containers, but the use of such would injure the appearance and qualities of the papain. The peculiar property of this enzyme is its solvent action for raw beef and the natives knowing this property have utilized it to their advantage. Even the leaves of the tree contain the enzyme and these foreigners have long been known to wrap a tough piece of meat in the leaves when, after a number of hours' contact, the meat becomes quite tender.

Knowing its solvent action upon raw proteid led me to consider meat as a means of standardization of the enzyme, and to be assured that I was working with the pure product I experimented with the fruit itself.

Several large paw-paws were prepared as follows: The green rind was first pared off, then the pulp was sliced into halves representing the inner and outer pulp respectively, and the seeds were collected. The juice was then expressed from these three different parts of the fruit, and the following test was then made upon these different juices.

Amt. acid		Amount		Part plant employed.	Amt. of beef.	Time of digestion.	Residue.
Amount 0.3 per juice.	0.3 per HCl	Amt. water.	0.1 per cent. NaHCO ₃ .				
Cc.	Cc.				Gms.	Hrs.	Cc.
10	75 cc.	none	none	juice	10	6	12
10	none	75 cc.	none	outer pulp	10	6	27
10	none	none	75 cc.	outer pulp	10	6	35
10	75 cc.	none	none	inner pulp	10	6	16
10	none	75 cc.	none	inner pulp	10	6	30
10	none	none	75 cc.	inner pulp	10	6	40
10	75 cc.	none	none	seeds	10	6	19
10	none	75 cc.	none	seeds	10	6	29
10	none	none	75 cc.	seeds	10	6	40

The test clearly illustrates two facts:

First: That in an acid solution the papain is the most active, the neutral media ranking second, and the alkaline third.

Second: That the enzyme of the juice of the outer pulp was much more active than that of the inner pulp or the seeds.

Upon the strength of the above test I herewith submit the test in full as applied upon papain.

Pass a quantity of round steak, which has been freed from all fat and gristle, through a meat chopper using the finest knife. Of this ground proteid carefully weigh 10 grams into a six-ounce bottle, weigh carefully 0.325 gram papain and brush into the bottle. Then add 85 cc. of 0.3 per cent. HCl, stopper the bottle,

mix well so as to break up the chopped meat, place the bottle in a water bath at 52° C. and maintain at this temperature for 6 hours, gently inverting the bottle every 10 minutes. At the end of six hours' digestion remove the bottle from the bath and pour the contents into a graduated settling tube. Let stand $\frac{3}{4}$ of an hour and then read the amount of undigested proteid left which should not measure over 2 cc. A papain which meets this test is reported as possessing an activity of 1 : 30 in 6 hours.

Some manufacturers claim that the test should be conducted in an alkaline media and that egg albumen should be used instead of raw beef; but to me this seems as absurd as to claim that pepsin should be tested upon starch in an alkaline media. The vegetable enzymes show the same selective peculiarities as do the animal enzymes, and the fact that the juice from the fruit shows its maximum activity in a 0.3 per cent. hydrochloric acid solution acting upon raw beef leads me to recommend this test as best suited for the assay of either bromelin or papain.

CONCLUSIONS.

To summarize, then, these digestive enzymes require more than that ordinary skill and experience in their assay.

We have seen by the foregoing:

First: That the composition of the white of the egg, chemically and probably even physically, when used for the assay of pepsin, has a great bearing upon the apparent strength of this ferment. The albumen seems to be more difficult to digest the first twenty-four hours after the egg is laid and a change gradually takes place until after about five to seven days it has reached its maximum solvent condition. After this period its digestibility gradually diminishes.

Second: In the assay of pancreatin for starch hydrolysis, as well as all the diastasic ferments, the kind of starch used is of prime importance and in stating the strength of each it should be in terms of the particular starch employed.

Third: The papain seems to be equally active on any kind of raw beef when acting in an acid media, but if the character of the beef is changed as, for instance, by cooking, papain loses its solvent action upon the proteid; and

Fourth: Rennet is influenced, in testing its coagulating power, by

The condition of the milk, its chemical composition such as the presence and quantities of inorganic salts, particularly those of calcium,

The manner of mixing the rennet with the milk;

The brand of cows from which the milk is taken; and lastly

The temperature at which the milk was kept before using and during the test.

PLANTS AND MACHINERY

THE MANUFACTURE AND PERFORMANCE OF THE EDISON STORAGE BATTERY.

By HOWARD LYON.

Received August 5, 1911.

Fifty years ago Planté demonstrated the possibility of using an electric current to do chemical work on plates immersed in an electrolyte and of obtaining a current again through reversal of the chemical process by connecting the plates by a conductor outside of the container. Such a cell behaves exactly as though it were some sort of a structure in which electricity could be stored as a reagent in a bottle, and thus it has become generally known as a storage battery. Until a very few years ago there had been no radical departure as to the nature of the plates and the electrolyte from the fundamental form assembled by Planté. The modern practical battery has continued to make use of lead plates and a sulfuric acid electrolyte.

The lead battery as developed since the time of Planté is open to serious objections, chief of which are the following: *First*.—Lead structures, by reason of bulk necessary for strength and a heavy electrolyte, make the weight of the battery excessive. *Second*.—The electrolyte (sulfuric acid) is intensely corrosive, and the nature of the liquid compels confinement in a fragile container. *Third*.—Physically the lead structures are weak and the pockets of lead oxide are weaker still. *Fourth*.—Secondary chemical activity is set up in a lead cell while standing partly discharged producing sulfate of lead instead of the useful oxides, so that in idleness there is a marked loss of electrical energy. *Fifth*.—The specific gravity of a troublesome electrolyte should be definitely maintained and the electrolyte should be rather frequently renewed. As a matter of fact the specific gravity of the electrolyte is constantly changing in the cycle of charge and discharge. *Sixth*.—Charging current exceeding a certain rather low amperage causes "buckling" of the plates. This loosens the oxide from the pockets and thus lessens the ampere capacity of the cell besides tending to produce short circuits. *Seventh*.—Such cells even in idleness must be charged at frequent intervals, for a discharged or partly discharged cell disintegrates rapidly.

Realizing the very great importance of the storage cell in modern electrical development and also the imperfections of existing types of batteries, Mr. Edison, about ten years ago, set himself to the task of producing a storage cell in which if possible the defects noted above might be eliminated.

Stated briefly the Edison Storage Cell makes use of steel grids holding perforated tubes containing nickel oxide and nickel flake for the positive plates and perforated box-like cases containing iron oxide for the negative plates, the plates being immersed in a solution of caustic potash containing a small per cent. of lithium hydrate enclosed in a steel can. All the

steel parts are protected by a specially durable nickel plate.

Commercial use of the later forms of the alkaline battery has abundantly demonstrated its practical efficiency for pleasure vehicles, trucks, and even omnibuses and cars. Chemical and structural durability is a phase of large significance as applied to this new energy-storing device. Durability and dependability are far more important qualities from the standpoint of the users of a storage battery than weight, cost, or efficiency, however desirable these latter qualities may be. *The truckman needs power not efficiency curves.* Durability is ensured by the mechanical construction of the Edison battery and by an electrolyte and active materials which remain unchanged with very moderate care. Dependability follows from the fact that in commercial service such treatment as a battery ordinarily receives will not change the nature or behavior of plates or electrolyte. The confidence of the manufacturers of the Edison battery is expressed by their guarantee that the capacity of the battery will be not less than 90 per cent. of the original capacity after three years of service when applied to commercial vehicles.

Commercial service inevitably means a likelihood of overcharge and discharge, and lack of attention to the electrolyte. This neglect in the Edison battery results merely in less immediate capacity, not in ruination of the cells.

Mechanically the cells are as stable as a well-made gas-cock. In fact they are so well made that the plates are confined in a container whose cover is welded in and all but hermetically sealed.

With renewal of electrolyte after each 250 complete charges and discharges, and addition of pure water from time to time to the electrolyte to make up for loss principally at the time of charging, and regulation of charging current according to experience based on careful recorded observation, there is no reason why the cells should not remain practically unchanged through a series of years. Combined with these qualities its weight, which is about half that of existing lead batteries of the same capacity, is such that a battery of sufficient capacity to propel a pleasure vehicle one hundred and fifty miles may be incorporated in what appears to be the natural and artistic body of the vehicle. In fact the electric pleasure vehicle has distinctly the appearance of a horseless carriage.

The Edison storage cell is at present being made in five sizes known as A-4, A-6 and A-8 together with two sizes for light work known as B-2 and B-4. These sizes differ only in the provision for active material and plate surface. The increase of weight for larger sizes is somewhat less than the increase of energy output. The following table gives the dimensions, weights, discharge rate and ampere-hour output for the three larger sizes:

	A-4.	A-6.	A-8.
Outside measurement of can in inches	2 $\frac{1}{16}$ X 5 $\frac{1}{8}$ X 12 $\frac{1}{2}$	3 $\frac{1}{8}$ X 7 $\frac{1}{8}$ X 12 $\frac{1}{2}$	4 $\frac{1}{8}$ X 10 $\frac{1}{8}$ X 12 $\frac{1}{2}$
Weight of complete cell in pounds	13.3	19.0	25.0
Normal discharge rate in amperes	30	45	60
Rated ampere hour output	150	225	300

These three types of cells have each the same height and require for clearance of pole pieces and connectors a compartment whose height is fifteen inches.

The following description which is distinctive for plate surface only, relates to a cell of type A-4.

All of the steel parts used for assembling the active elements as well as the can itself and the connecting bolts, nuts and washers are nickel-plated. After the plating process the parts are placed in sealed carbon-lined retorts arranged for the passage through of hydrogen gas during the process of annealing, which is accomplished with intense heat. By this process the nickel-plating is incorporated as a firm part of the steel surface itself. No amount of bending will cause it to peel. For both positive and negative plates the frames or grids for holding the cases containing the active materials are blanked out of sheet steel, leaving openings of such size as to accommodate the required number of cases. The positive plate consists of thirty tubes in two rows. These tubes are about four inches long and one-fourth of an inch in diameter and are made of spirally rolled perforated steel ribbons, lapped and locked at the edges and reinforced by steel bands. The perforations in the walls of the tubes permit the moistening of the nickel hydrate with the electrolyte. The ends of the tubes are flattened so that they may be assembled and clamped down by tongues on the steel grid.

The filling of the tubes for the positive plate is a most interesting one and is a triumph of inventive ingenuity. Machines have been designed to automatically fill rows of tubes and tamp the nickel hydrate and flake nickel which are fed in alternately in such quantities as to make layers approximately $\frac{1}{100}$ of an inch in thickness for the nickel hydrate and a less thickness for the nickel flake. The nickel hydrate which is in no large measure conductive is thus brought into intimate reach of current action by thin layers or disks of nickel. In testing the distribution of active and conducting material a number of tubes are selected at random from a certain output. Cross-sections are made and the conductivity or contact of nickel flake with the walls of the tube is determined by use of a microscope and a metal stylus which is touched to successive layers with the result that an

indicator gives proof of connection. Thus the number of poor connections is determined and counted. The filling is so carefully done that contact is ensured in 97 per cent. of the layers. The flake-nickel is prepared as follows: With a total thickness of a sheet of paper two hundred and fifty alternate layers of copper and nickel are deposited electrolytically on rotating drums shifted by traveling cranes. These cylindrical sheets are stripped off and cut up into squares about one-sixteenth of an inch in diameter. The squares are treated with ammonia in a retort and the copper dissolved and leaving only the very thin nickel flakes. The nickel flakes when washed and dried is so light that it floats in the air. There are 300 nickel hydrate units in each tube, 9000 in each plate and 36000 in an A-4 cell.

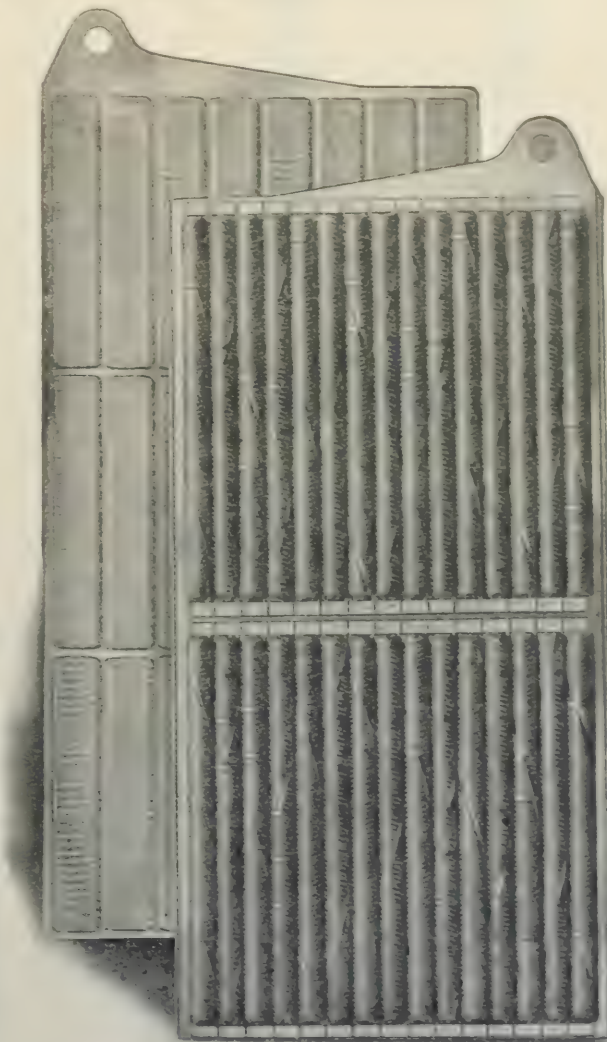


Fig. 1.

The iron-oxide for the negative plate is enclosed in twenty-four perforated rectangular flattened pockets crimped into place in the grids by powerful pressure. Mercury oxide added to the iron-oxide serves the same purpose in making it conductive as does nickel flake for the nickel hydrate layers.

The grids as assembled above are very light and strong, suited to withstand all shocks to which such a structure would be subjected in commercial use. Each cell of the A-4 type contains four positive and five negative plates assembled alternately with the negative plates outside. Hard rubber rods are used to space the plates. Rubber pieces also insulate the plates at the sides, edges and bottom from the steel can. The pieces of broad hard rubber at the bottom lift the plates enough above the steel surface to make a space for sediment, although in the Edison cell any deposit at the bottom of the cell will be almost wholly

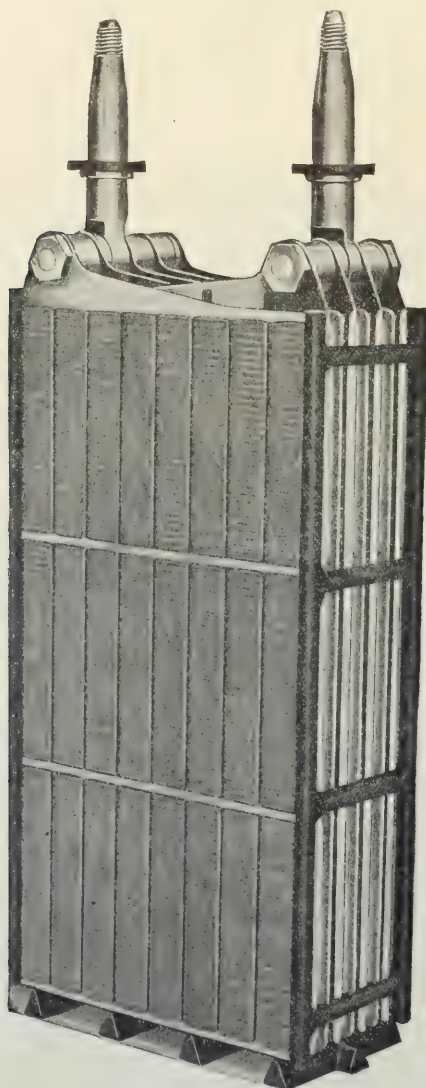


Fig. 2

such as would adhere to the outside of the plates and to the walls of the perforated containers during loading. The plates of the positive and negative groups are respectively fastened by nuts to horizontal steel rods integral with the positive and negative pole pieces and distanced by steel washers. Thus assembled with the insulating pieces the elements are enclosed in a corrugated steel can.

The cover of the can has four mountings. Two

of the openings are of the pole pieces, a third for the separator valve which permits the escape of gas when charging but prevents spraying, evaporation, and the spilling of the electrolyte. The fourth opening is for the purpose of adding water to replace that carried off in charging and is fitted with a cover that may be clamped down and made water-tight by a locking lever. The positive and negative terminal posts are tapered to fit terminal lugs, the posts being insulated from the cover by hard rubber washers and bushings. Soft rubber packing is used about the terminals to prevent leakage or creeping of the salts.

The packing ring is held down by a hard rubber nut threaded into a pocket of the cell cover.

When the cover has been properly assembled with the plates in the steel can, it is welded at the edge to the can itself by the oxyacetylene flame, and thus the can is in effect, a box of seamless steel. The corrugations of the can give maximum rigidity for a given weight or thickness of material. The cells are assembled into a battery in strong bent-wood trays and insulated and spaced from one another by hard rubber buttons which extend through the sides of the trays and fit over embosses pressed out on the sides of the steel containers. Blocks in the bottom of the tray fit into the flanged bottoms of the cells from which they are insulated by soft rubber pads. Steel terminal lugs fit the tapered pole pieces and cells are electrically connected by nickel-plated copper links swedged into the lugs.

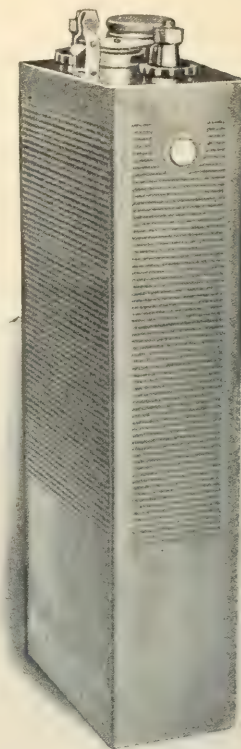


Fig. 3.

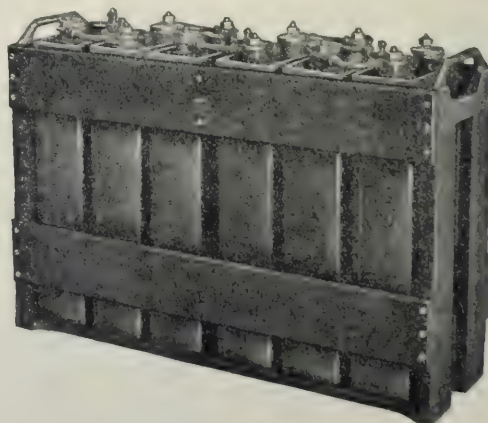


Fig. 4.

The A and B type of cells were evolved from the earlier type E in which flake graphite was used in the positive plate to make the active material conductive. The graphite slowly oxidized and swelled and the change resulted in a diminished capacity for the cell. In the later evolved battery conduction (in the positive plate) is secured as already stated by nickel flake. Although thousands of the type E cells had been put upon the market, the manufacture of these cells was discontinued for four or five years, during which time at an expense of over two million dollars many thousand experiments were made to improve the positive element. These experiments resulted in the nickel flake and hydrate unit previously described. Rarely indeed has inventive activity been applied more vigorously or persistently to overcome difficulties than in the case of this later development of a practical storage battery. Indeed this accomplishment, measured by the skill applied and the far-reaching value of the product, may well be rated as the crowning achievement of a great inventor.

A comparison of weights of lead cells and Edison cells of the same capacity without trays shows about one-half the weight for the latter type. The space occupied by an A-4 battery with its holder is somewhat less than that of a lead battery of equal energy capacity.

Less dead weight to be carried and less space requirement for battery means a vehicle of lighter construction and consequently greater mileage capacity for the lighter and less bulky type. The normal working voltage of the Edison battery is 1.2 as compared with 1.96 volts for the lead cell. Hence for a given voltage the number of cells of the Edison and lead type required would be as 13 to 8. In the comparisons of weight and bulk this fact has of course been taken into consideration.

The first cost of a lead battery is less than that of the Edison type, but when durability is taken into consideration the added cost of renewals and maintenance for the lead battery would make a total much exceeding the initial cost of an Edison battery. Users of lead batteries have been troubled by the fact of a steadily lessening capacity with even one year's use. The Edison battery is guaranteed to retain practically its initial capacity after three years of service, such as is required in trucking.

The nature of the care required for the Edison battery is simply addition of distilled water to make up for charging loss, the renewal of the solution at infrequent intervals and charging according to use. No attention *can* be given to the plates for they are entirely inaccessible.

The lead battery must be charged whether in use or idleness. Charging a lead cell beyond its normal rate causes rapid deterioration. The rate of charge for an Edison cell is practically limited only by the temperature developed which should not exceed 105° F. The limited mass in plates and electrolytes of course makes the regulation of the charging rate necessary. However, the steel cans transfer heat

to surrounding air while the containers for the lead type are heat insulators.

The Edison cell has a somewhat higher resistance than the lead cell, and for this reason in hill-climbing the lead cell would have a seeming advantage in the fact that it would be possible to call upon the battery for greater current to carry the vehicle over the hill. This is only a seeming advantage, for the Edison cells and vehicle may be lighter, so that there will be less work to do and further the lead battery is structurally limited in its current output. An overcharge is distinctly destructive to its elements.

It means little to say that the lead cell is more efficient pound for pound when *new*, for the cell does not retain the initial advantage long after it is put in service. It is harassing to a user of an electric vehicle not to be able to hasten the charging rate to complete a journey. The Edison cell permits this treatment and even shows a gain of efficiency. Furthermore, the driver of an electric vehicle using the Edison battery may definitely know before he starts on his journey whether or not the current will hold out. With a given charge he is able to depend upon a given capacity by reason of the dependable character of the battery. A feature of value in relation to the Edison battery is that the capacity of the cells becomes greater with use. Overcharging expedites this betterment of the battery and is recommended by the manufacturers.

It would be manifestly out of place to attempt to discuss, within the limits of this article, the curves that have been plotted to show the behavior of the battery under various conditions favorable and unfavorable.

A full discussion of this subject may be found in the paper of Mr. Walter E. Holland read at the 26th annual meeting of Edison Illuminating Companies September 6-8, 1910.

An idea of the nature of laboratory tests as applied to the Edison battery may be obtained from the following description of typical curves and from conclusions based on the inspection of the curves. Effect of normal and overcharges for a battery after having covered 17,000 miles in a one-ton delivery wagon.

Plates Nos. 5, 6, and 7 show in a graphical way what happens to cells which have been subjected to various sorts of treatment, and especially to the treatment which has been known to be destructive to other types of storage cells. The legends accompanying the plates referred to show the nature of the laboratory test, and an inspection of the curves tells at a glance the result of various treatments.

An inspection of the curves of charge and discharge (Fig. 8) for an Edison cell shows an efficiency of 60 per cent. to 65 per cent. A new lead cell shows an efficiency of 75 per cent. to 80 per cent. but this efficiency falls off very rapidly when the cell is put into use, while the Edison cell shows a gain in efficiency. One particular Edison battery that had given a total of 20,000 miles in delivery service showed a gain in efficiency.

The statements of the writer as related to the lead

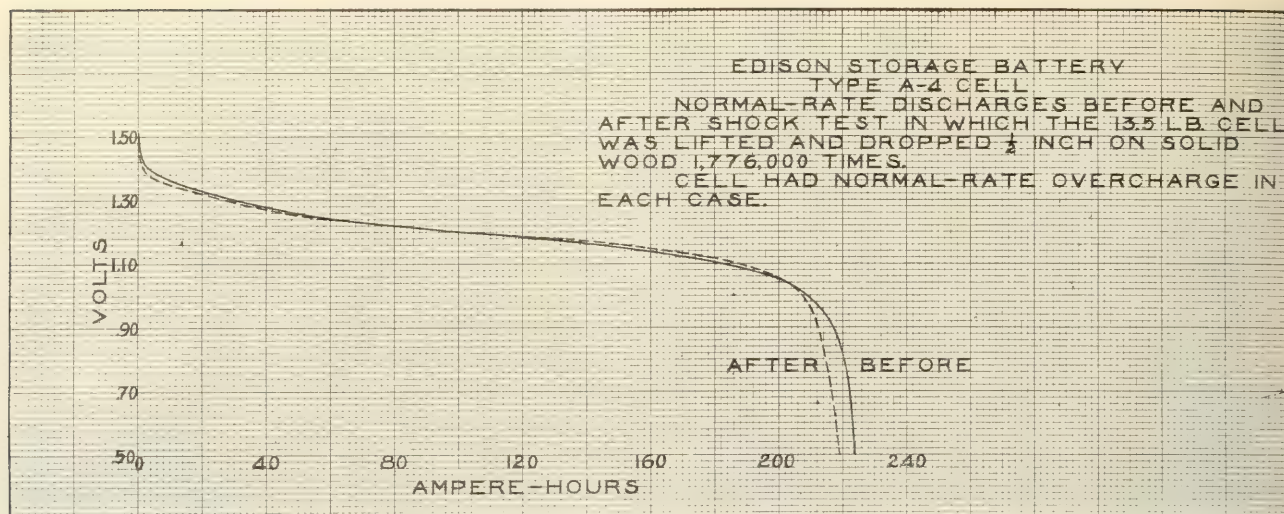


Fig. 5.

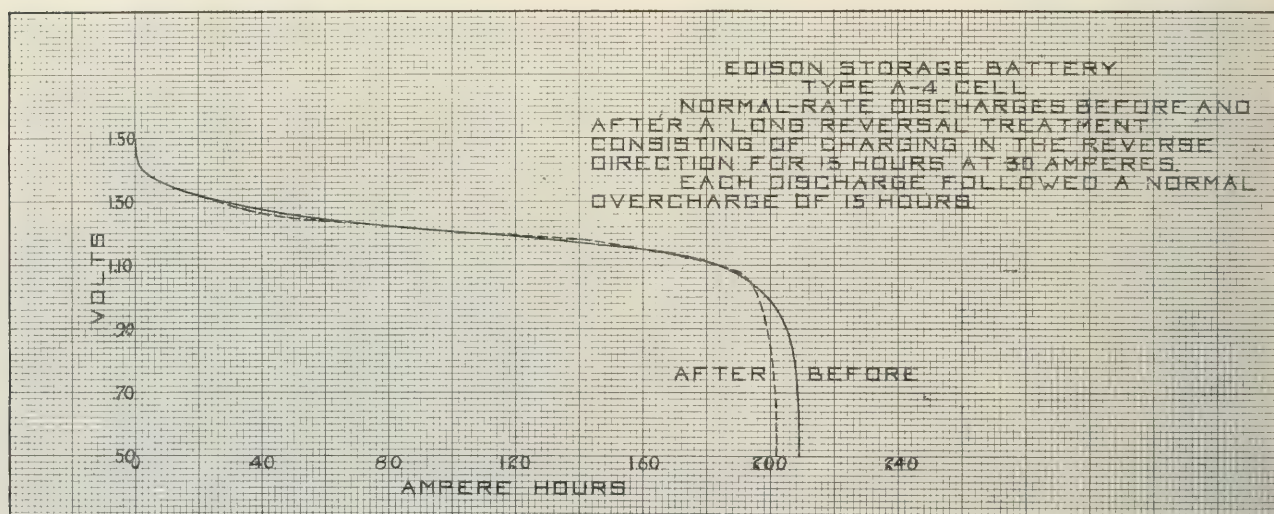


Fig. 6.

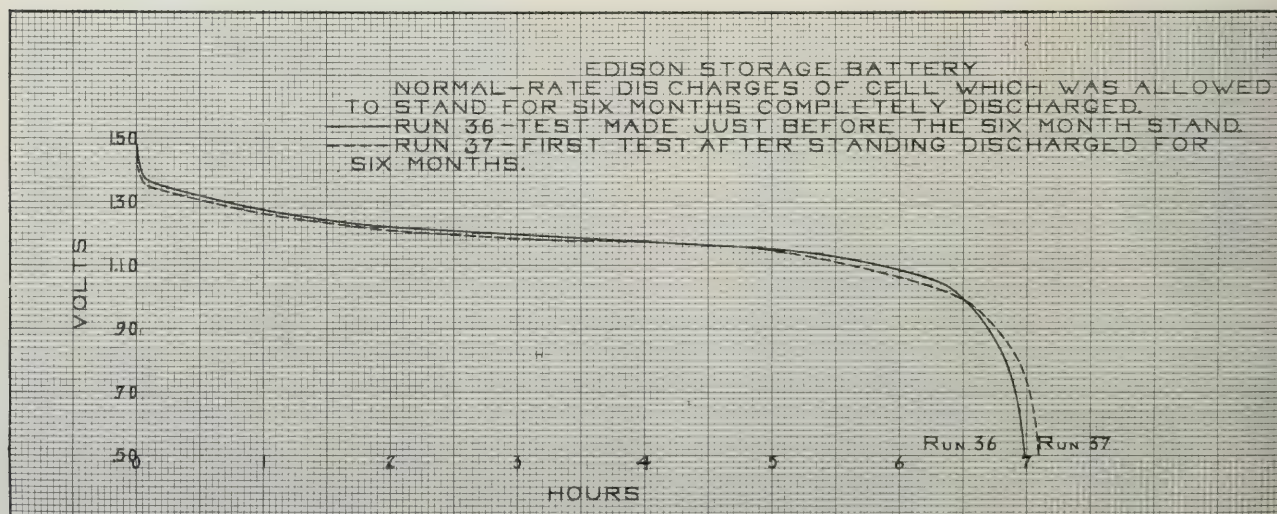


Fig. 7.

cell are based upon fifteen years of experience in use of the cell, while experience with the Edison cell of course does not extend over such a length of time. There is ample proof, however, of its much greater reliability, first in the evidence of the behavior of the battery in commercial use and secondly in the results of laboratory tests.

Efficiency is an exceedingly desirable quality in

it would eventually displace every form of battery in present use.

According to the results of trial runs, it would appear that electric pleasure vehicles equipped with Edison cells should no longer be classed as town cars. This statement is made by the Edison Company.

"One hundred miles to the charge is quite ordinary, a hundred and fifty miles easy, and runs of over two

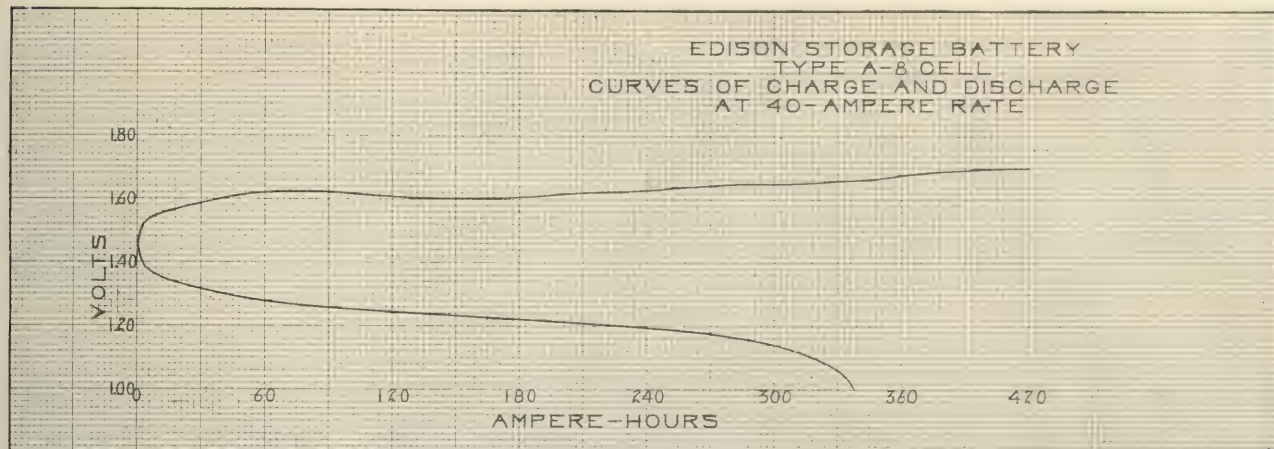


Fig. 8.

an energy-storing device, but granted even fair efficiency the availability of the stored energy after one month, six months or a year is a matter of paramount importance. Efficiency means little in economy if the structure of the device is not sturdy. As in the case of investments, a possible high rate of interest cannot be considered with the lower per cent. that can be anticipated with certainty. In relation to the first cost of this battery taken with its permanency, Mr. Edison said in effect that the cost may be con-

hundred miles have been made." This, of course, means on a single charge.

An electric vehicle was propelled nearly to the top of Mt. Washington but finally had to turn back on account of a storm. Confirmation of the assertions in regard to dependability of the Edison battery is best furnished by experience of Express Companies, Department Stores, and large retailers who have hundreds of delivery wagons in daily use. The value of this type of energy storage is still better shown

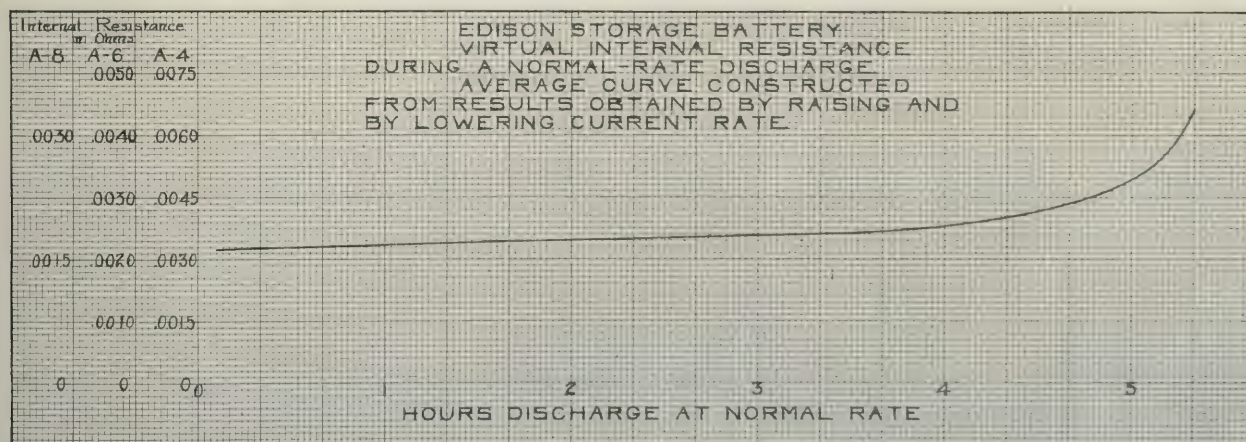


Fig. 9.

sidered as an investment, not as a running expense.

The feature of the Edison cell that must appeal to all who use battery current for any purpose is that we have finally in portable form a store of energy that is ready for use at any moment and that may be held indefinitely without material waste. As soon as its merits become generally known it would seem that

by its application to cross-town car propulsion in New York and to omnibuses and drays, a type of service that is most exacting. Two leading Express Companies have in use at the present time one hundred and seventy five delivery wagons equipped with Edison batteries.

The purchaser of an electric vehicle surely need

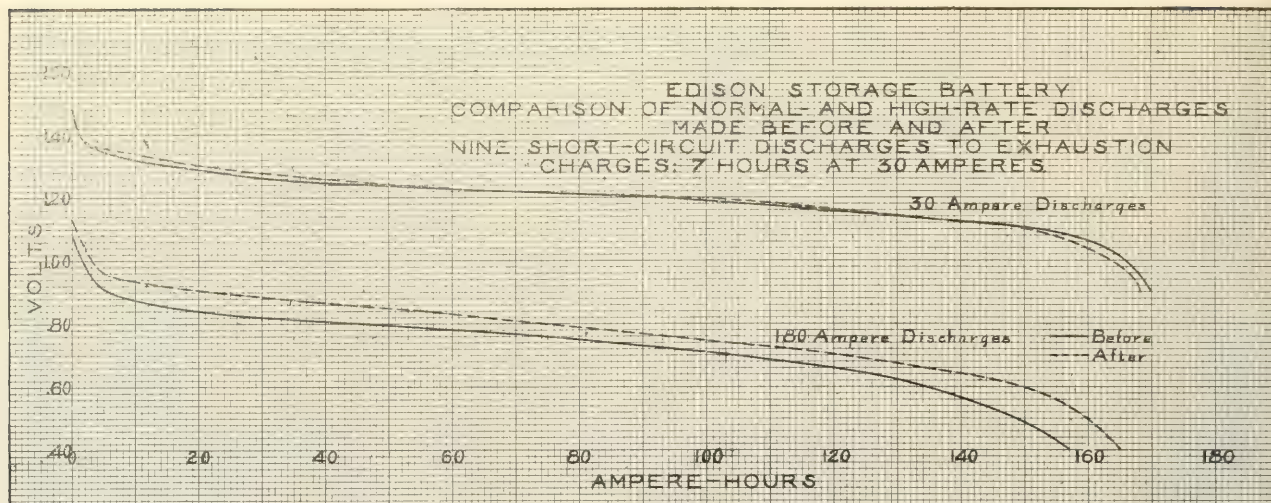


Fig. 10.

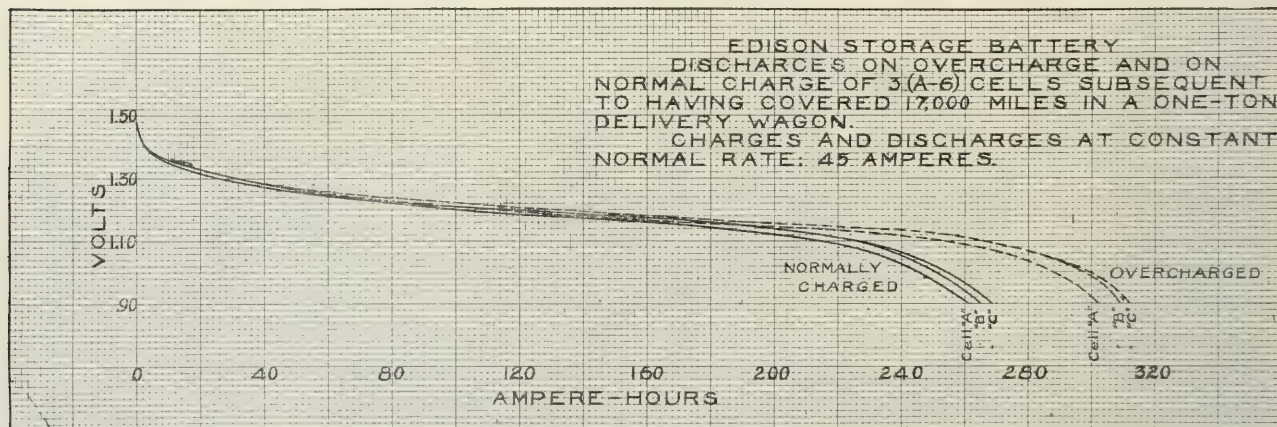


Fig. 11.

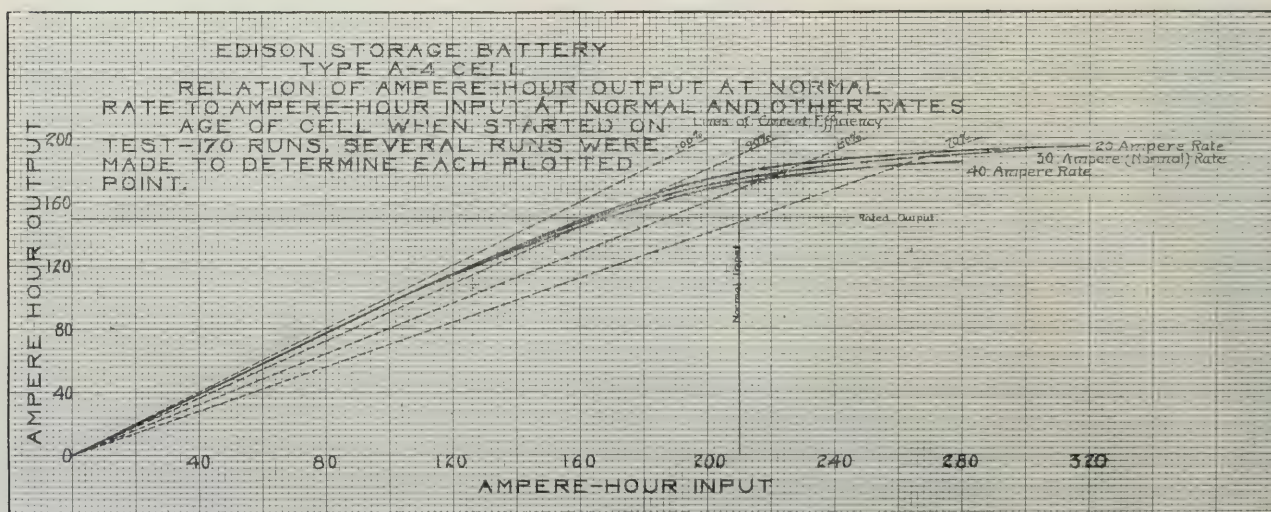


Fig. 12.

not hesitate to purchase an Edison battery, fearing that the battery may not be durable, for one manufacturer of electric vehicles absolutely guarantees to replace anything that goes wrong in the battery up to 50,000 miles of travel.

The history of the method of development of the Edison storage battery is most interesting. In answer to questions of the writer, Mr. Edison stated that all possible chemicals and structure that had been used or could be used for plates and electrolytes were considered at the outset, and cells were made up one by one as knowledge and imagination prompted the selection. Every cell was carefully tested and the behavior recorded. He said: "We had as many as eighteen hundred distinct types of cells on test at one time. We did not construct a few cells and wait a year or two for results, but crowded into the period of observation experience with thousands of cells." Finally he said with emphasis: "An individual's lifetime is far too brief to attain any marked advance in invention unless he extends his experience simultaneously to a very wide range of materials, structures and phenomena. An investigator like Luther Burbank has a great advantage over me for he can carry on millions of experiments at the same time."

The Edison battery is the result practically of the efforts of one man expended almost continuously over a period of eight years and personally directing many thousand experiments which were made. By this I do not mean the battery in a broad and general sense, but I mean the precise mechanical and chemical structure that it now is to-day, and not only that, but practically all machinery and appliances used in its manufacture are the results of Mr. Edison's personal suggestions and supervision. He has had loyal, devoted, and hard-working assistants who have carried out his ideas with enthusiasm, but it is the Edison battery with which we are now dealing, both in fact as well as in name. In the years to come I believe it will be regarded as the greatest monument to his genius, and if the full story of its development were told, I believe it would represent one of the greatest intellectual accomplishments of all time.

AN ELECTRIC HEATER FOR ETHER EXTRACTIONS.

By WILLIAM H. ROSS.

Received September 26, 1911.

Many electrical appliances have been devised for laboratory use, but up to the present illuminating gas, where available, is used as the principal source of heat in most laboratories. This is largely due to the fact that electricity is ordinarily more expensive than gas, and for many purposes not so convenient, since changes in temperature can not be brought about as quickly in an apparatus heated with electricity as with gas. This is true particularly of electrically heated hot plates, or electric heaters for Kjeldahl work.

In the case of electric furnaces, on the other hand, these disadvantages are not so serious. The necessity of bringing about quick changes in temperature is

not so important, and as the apparatus may without much inconvenience be surrounded with a very thorough heat insulation, a furnace of this kind may be used very economically. A simple furnace for high temperature work has recently been devised by Benner and may be made with little expense.

In an electric heater for ether extractions the disadvantages already referred to are still less serious. Owing to the low temperature required the expense of heating is immaterial, and a uniform, rather than a variable, temperature is desired. Furthermore, an apparatus of this kind has the advantages of safety and neatness over the gas-heated water bath which is still largely used for this purpose.

The heater herewith described has been in use in this laboratory for some time, and has proved very satisfactory both in the matter of convenience and efficiency.

The outer part of the heater, which is represented in Fig. 1, consists of a rectangular box, 80 × 20 × 12 cm., made of ebonized asbestos, 1 cm. in thickness. The asbestos serves the double purpose of lessening the loss of heat by radiation, and does away with any danger of short-circuiting between the wire system shown in Fig. 2, and the outer box. The box is supported on brass legs, 4 cm. in length.

A galvanized sheet-iron box, B, 74 × 18 × 5½ cm., rests on asbestos supports within the outer box, and at a distance of 2 cm. above the wire system which is supported horizontally on asbestos supports about 2½ cm. above the bottom of the outer box.

The top T of the outer box, which is made of the same material, is detachable from the rest of the apparatus, and has six openings through which the flasks of the extracting apparatus pass, and rest on the bottom of the iron box below. When the current is turned on by means of a switch, S, at the end of the outer box, the flasks not only become heated by contact with the iron support upon which they rest, but are surrounded with a heated atmosphere which minimizes the current required to bring about the extractions. Asbestos covers, C, are provided for the holes which may not be in use. If desired, split covers, SC, may be obtained to fit closely around the necks of the flasks. These are not at all essential, however, as the current necessary to bring about a given rate of extraction is decreased but little by their use.

By means of the regulating switches S₁ and S₂, the current flowing through the apparatus may be varied from 1 to 5 amperes. This is brought about by cutting out the outer strands of wire as the switches are moved from position 1 to position 5. As the strands are strung in the form of spirals, any expansion which takes place on passing the current causes no noticeable lateral displacement of the strands, but simply causes the coils to move a little closer together. Any danger of the strands coming in contact, however, is prevented by separating them with strips of asbestos as shown in Fig. 1.

Brass rods, R, 11 mm. square and 74 cm. long, lie along the sides at the bottom of the outer box

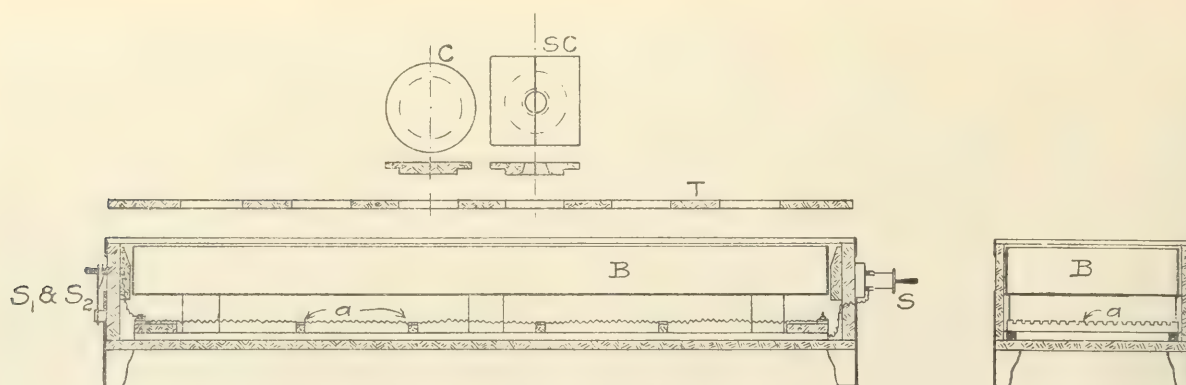


Fig. 1.

and serve the double purpose of giving rigidity to it, and of connecting the electric circuit with the wire system shown in Fig. 2.

Owing to the small current required in making extractions with ether, it was not thought advisable to provide for heating less than six flasks at a time. The resistance wire is made of No. 22 nichrome alloy which affords a resistance of 0.937 ohm to the foot.

When the apparatus is connected with the 110-volt circuit, the strength of current obtained and the length of wire through which the current passes at

The minimum temperature obtained with the top plate removed and glycerine in the inner box is 60°. This increases to 80° with the plate in place, while with the switches in position 5 a maximum temperature of 135° may be obtained.

The apparatus as thus described may be obtained from the Central Scientific Co. at a very moderate cost.

The advantages of the apparatus may be stated as follows:

(1) The flasks rest on a hot metallic plate, and are surrounded by a heated atmosphere in consequence of which a very low current is sufficient for extractions with ether.

(2) The temperature of the apparatus is capable of being changed between considerable limits which enables the same apparatus to be used for making extractions not only with ether, but also with acetone, chloroform, carbon tetrachloride, and other solvents commonly used in making extractions. The same feature enables the apparatus to be heated up quickly at first then used for making extractions with ether.

(3) After the extraction is complete, the solvent may be evaporated from the flasks without danger of ignition by replacing them in the apparatus and turning on a low current.

(4) With the top plate removed the apparatus may be used as a hot plate for making slow evaporations, and for other purposes.

(5) If so desired it may be used as a liquid bath by placing water, or some other high boiling-point liquid, in the inner box.

AGR. EXPT. STATION,
UNIVERSITY OF ARIZONA,
TUCSON.

TWO NEW PIECES OF CHEMICAL APPARATUS.

- I. Apparatus for the continuous extraction of liquids with immiscible solvents lighter than water.
- II. Apparatus for quantitative reactions which depend on the measurement of an evolved gas.

By R. F. BACON AND P. B. DUNBAR.

Received September 26, 1911.

I. CONTINUOUS LIQUID EXTRACTOR.

This apparatus was designed originally for use in the extraction of lactic acid from ketchup and other fruit products. Its principal advantages are com-

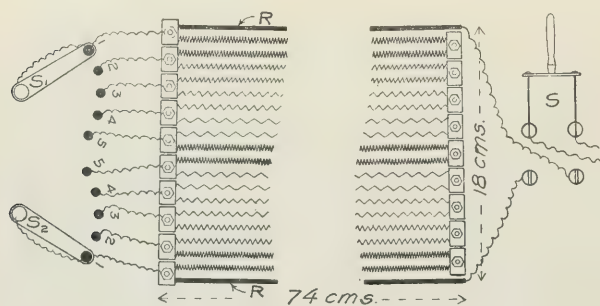


Fig. 2.

each step as the switches are moved from position 1 to position 5 are as follows:

Position of switch.	Number of strands in circuit.	Total resistance. Ohms.	Length of wire. Cm.	Current. Amp.
1	18	110.0	3578	1.00
2	14	73.3	2384	1.50
3	10	55.0	1789	2.00
4	6	40.0	1301	2.75
5	2	27.5	895	4.00

By changing the switches one at a time, twice the number of steps in the variation of the current may be obtained.

The inner vessel is water-tight and may be used as a liquid bath if desired. When used as a water bath with the top plate removed, the water becomes heated to a temperature of about 42° with the switches in position 1. This causes the ether to distil at almost exactly the same rate as when the apparatus is used as an air bath with plate P in place. When it is desired to heat more than six flasks at a time, this can be conveniently done by removing the top plate, in which case the apparatus can be more economically used as a water bath.

pactness, the elimination of ground joints and stoppers, and practically complete condensation. Seven of the extractors may easily be placed side by side on a 24-inch hot plate. They have been made for the authors at a cost of \$1.50 each, but may be constructed in the laboratory by any one having ordinary skill in glass-blowing.

The apparatus consists of four parts: (1) A jacket flask; (2) an extraction thimble; (3) an ordinary Gooch funnel; (4) a condenser.

(1) The jacket flask (Fig. 1) A is made of glass tubing 2 inches in diameter and approximately one-

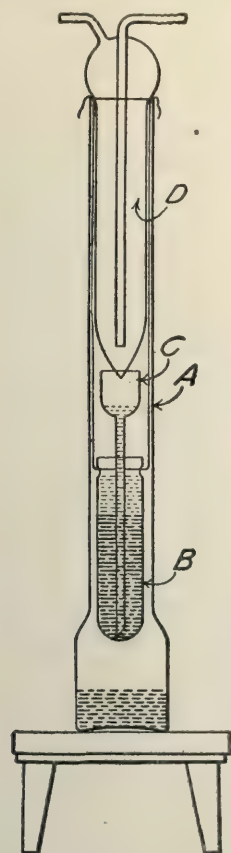


Fig. 1.

The open end is flared somewhat to permit the tube to hang in the jacket. The condenser is closed by a two-holed rubber stopper, through which pass the in-flow and outflow tubes.

OPERATION.

Place from 100 to 150 cc. of ether in the jacket flask A; put the liquid to be extracted (100 cc.) in the test tube B, insert the funnel in the same tube and suspend it in the jacket flask, about 3 inches above the bottom, with a copper wire which passes through the holes in the test tube and is hooked over the rim of the jacket flask. Insert the condenser in the top of the jacket flask. The condensation is usually so perfect that no ether vapors escape into the room. The condensed ether drops from the point of the condenser into the funnel and is carried to the bottom of the test tube whence it flows up through the liquid and overflows at the top.

The efficiency of the extractor may be increased by the use of a glass spiral attached to the stem of the Gooch funnel, as described by Kempf.¹

II. APPARATUS FOR THE MEASUREMENT OF AN EVOLVED GAS.

The apparatus represented in Fig. 2 was devised to give in a compact and easily manipulated form an apparatus which will allow of the measurement of an evolved gas without first sweeping out all air or other indifferent gases. It consists of a graduated funnel tube, A, a reaction chamber, B, an absorption tube, C, filled with glass beads, a eudiometer, D, and a leveling tube, E. A heating coil may be wrapped around the reaction chamber B when desired. The absorption tube C, which is sealed onto the eudiometer, fits into the reaction chamber B by means of a ground joint at F.

The manner of using the apparatus may best be illustrated by one of the reactions which can be advantageously carried out in it. Spica² estimates citric acid from the carbon monoxid evolved by decomposing this acid with strong sulphuric acid at 100° C. He runs air-free carbon dioxid through a flask containing the citric acid until all air is displaced from the apparatus. He then adds concentrated sulphuric acid, heats to 100° C., drives over the evolved carbon monoxid with a stream of air-free carbon dioxid, and collects the gas in a eudiometer over a sodium hydrate solution. The method as carried out by him is accurate, but requires considerable care and attention to remove the air from the apparatus completely, to insure that all evolved carbon monoxid is swept over into the eudiometer, and to prevent the strong sodium hydrate solution from sucking back into the reaction flask containing carbon dioxid and sulphuric acid. In the apparatus proposed by us no attempt is made to remove the air before reaction, the volume of evolved gas being simply measured by the increase in volume of the total gases after reaction. Thus the Spica method as carried out in this apparatus is as follows:

Place about 0.2 gram of citric acid in the reaction chamber B, open the stopcock X and bring the liquid (in this case a strong sodium hydrate solution) to the zero mark G in the eudiometer tube by raising or lowering the leveling tube E. The air in the apparatus is then at atmospheric pressure. Close X. To A add about 15 cc. of concentrated sulphuric acid. Lower the leveling tube so that the air in the apparatus is under reduced pressure. By carefully opening the stopcock X run in exactly

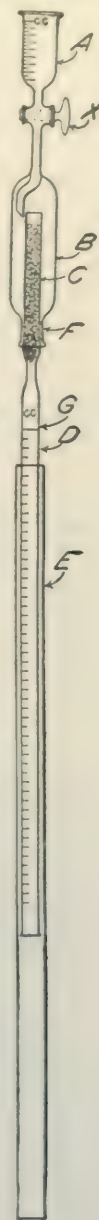


Fig. 2.

¹ Chem. Ztg., 34, 1365 (1910); C. A., 5, 1350 (1911).

² Chem. Ztg., 34, 1141 (1910).

10 cc. of the sulphuric acid. Close X and heat to about 100° C. by means of the heating coil until the reaction is complete. Let the apparatus stand until the absorption of other gases (sulphur dioxide, etc.) is complete and it has reached room temperature. Bring the gas in the apparatus to atmospheric pressure by means of the leveling tube E. The gas reading in the eudiometer minus 10 cc. (for the added sulphuric acid) equals the volume of the evolved gas at the existing temperature and pressure. The apparatus has been used in this laboratory with accurate results to estimate citric acid by the Spica method and for the estimation of amino acids by the Van Slyke method,¹ which depends on the evolution of nitrogen, by the action of nitrous acid on the amino acids. The apparatus is readily cleaned by taking it apart at the ground joint F.

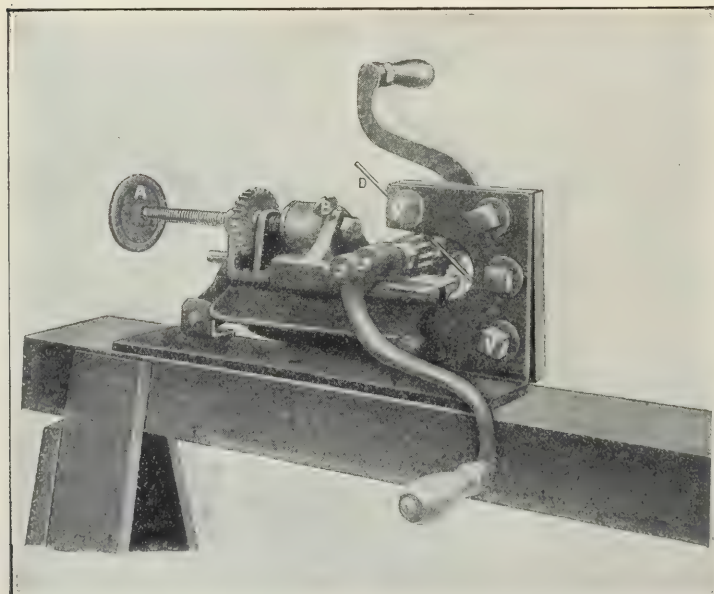
BUREAU OF CHEMISTRY,
WASHINGTON, D. C.

LABORATORY MILLING MACHINE FOR SAMPLING STEEL.

By CHAS. MORRIS JOHNSON.

Received November 1, 1911.

In certain kinds of steel the writer encountered much difficulty in getting samples of sufficiently



small mesh for the determination of carbon by the direct method described by him several years ago.

(“The Chemical Analysis of Special Steels”—John Wiley & Sons, 1909.)

The trouble was confined to thin sheets, wire, hack saw steel, band saw steel, razor blades, resistance ribbon, nails and small samples of all kinds that are irregular in shape and difficult to hold in the drill press vise.

The machine shown in the illustration afforded a successful means of avoiding various time-consuming expedients.

The sample D of wire, for example, is held in the vise V-V. The millings are taken up by means of a cutter, made of the best high-speed steel, and are caught on a piece of cardboard at C.

The automatic feeding device at A is hastened in its action by tightening the screw at B.

If desired, where a large number of samples are to be milled, a small motor can be used, and a pulley can be attached instead of one of the handles.

The milling cutters can be sharpened several times.

It is desirable, and well worth the small amount of time involved, to anneal all samples received, if they are not already in a softened state. This operation can be done in a half hour's time by heating the sample to 800° C. (bright red), quenching at once in water and then holding at 620°–630° C., for 20 minutes (low red). The annealing of 13 per cent. manganese steels has also been previously described in “Analysis of Special Steels, etc.” together with the chemical tests for perfect annealing.

The millings obtained by this laboratory tool are not sifted, as they are just right for direct determination of carbon by combustion in oxygen.

If the sample submitted is sufficiently rigid, it does not need to be held by both ends, as in the case of the sample of wire.

This machine, as illustrated, has been in use in the writer's laboratory for a year. Since its introduction, the samplers no longer dread the appearance of wire and steel ribbon, this work being now a mere matter of easy routine.

The first cost was a bagatelle compared to the saving of labor in one month. Several copies of this milling tool are now in use in other laboratories of this Company.

LABORATORY OF PARK WORKS,
CRUCIBLE STEEL COMPANY OF AMERICA,
PITTSBURGH.

ADDRESSES.

RECENT DEVELOPMENTS IN BAKELITE.²

By L. H. BAEKELAND.

Received November 13, 1911.

My subject involves the use of two main raw materials, phenol or carbolic acid, which is found in

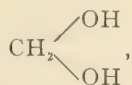
¹ *Ber. d. chem. Ges.*, [3] 43, 3170 (1910).

² Read at joint meeting of New England Section, Amer. Chem. Soc. and Soc. Chem. Industry, Boston, Nov. 10, 1911.

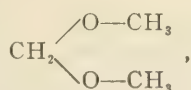
gas tar, and formaldehyde. The latter is now manufactured by the oxidation of wood-alcohol.

I should state that the name of formaldehyde is used in a rather broad sense. I never have seen real formaldehyde, CH₂O, and very few chemists have had occasion to examine it. It is a gas which can be made to liquefy and solidify by the intense arti-

ficial cold attainable by means of liquid air.¹ Solidified CH_2O melts at -92°C . The commercial product, designated ordinarily under the name of formaldehyde, is a watery solution of formaldehyde, containing at the same time variable proportions of methylalcohol. In these solutions, formaldehyde is present partially as methyleneglycol,

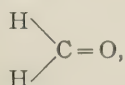


and as methylal,

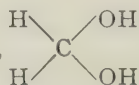


accompanied with variable amounts of several distinct polymers of formaldehyde, of polymers of methyleneglycol, or polymers of partial anhydrides of methyleneglycol, more or less directly related to paraform, trioxymethylen and similar substances.

The thermochemical researches of Delepine² had already shown, in watery solutions, the existence of stable hydrates, which are not decomposed by distillation, and the later work of Auerbach³ leave no further doubt on the very complicated composition of so-called formaldehyde solutions. The latter are merely mixtures of various chemical compounds which ultimately react in the same way as CH_2O , and which, for practical purposes, are equivalents for each other in the chemical reactions where formaldehyde or methylen-compounds are used. The main point in all these reactions is that the group methylen $=\text{CH}_2$ should exist in a mobile condition. It matters little whether this group $=\text{CH}_2$ presents itself as true formaldehyde or oxymethylen,



or as its hydrate as methyleneglycol,



The same remark applies to its polymers, paraform, trioxymethylene, or other polymers of formaldehyde, or polymers of methyleneglycol, or partial anhydrides thereof. All these substances can be substituted for each other, and the final result of the reaction can be made practically the same.

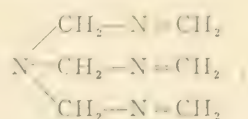
So well was this known that the early work of Ad. Baeyer and his pupils on condensation products of phenols and formaldehyde was carried out by means of the latter's methylen representatives: methylal, methylenacetate, methylenchlorid, or methyleniodid, for the simple reason that commercial formaldehyde was unavailable at that time.

¹ Raikov, *Chem. Ztg.*, **26**, 135; **12**; **11** (1901). Kekule, *Ber.*, **25**, 2435. Harries, *Ber.*, **34**, 635.

² *Compt. rend.*, **124**, 1454; *Bull. soc. chim.*, **17**, 849.

³ F. Auerbach, also Auerbach and Barschall, *Arb. kais. Gesundh.*, Band XXII, Heft 3 and Band XXVII, Heft 1, Verlag Julius Springer, Berlin.

Ammonia combines very easily with formaldehyde and forms hexamethylenetetramin,¹



So eager is the tendency of combining with ammonia, that if formaldehyde, or any of its equivalent compounds, which keep the group CH_2 in mobile condition, is put in presence of an ammonium salt, like ammoniumchlorid, acid is expelled, and hexamethylenetetramin is formed.²

Consequently, whenever an excess of formaldehyde or a formaldehyde compound is put in presence of ammonia or an ammonium salt, hexamethylenetetramin is formed forthwith, so that mixtures of ammonia and formaldehyde, or hexamethylenetetramin, are practically the same thing. On the other hand, hexamethylenetetramin, in presence of acids, reliberates easily formaldehyde. There is nothing astonishing that in the condensation of phenols and formaldehyde we should be able to replace formaldehyde by other related compounds.

Let it then be understood that in the reaction I am about to explain, whenever I refer to formaldehyde, this broad denomination includes many substances which are practically equivalent in their chemical action to the orthodox, but elusive true formaldehyde, CH_2O .

When phenol is acted upon by means of formaldehyde, or its equivalents, a most varied set of reactions can occur; even by starting from the same raw materials, new substances may be produced which, according to conditions of operation, may vary, considerably in appearance, as well as in chemical and physical properties.

The earlier investigators, like Ad. Baeyer and others,³ were especially on the lookout for substances of definite chemical constitution, which could be easily isolated, crystallized and purified for the development of their purely scientific work; if they obtained non-crystalline bodies, of resinous appearance, this was merely considered as a drawback, and constituted an unpleasant obstacle in their theoretical research work. Their resins did not seem to attract much of their attention, and the study of the resinous products was soon abandoned in favor of the crystalline bodies which could be obtained. Under the circumstances, it is quite natural that no special effort had been made to produce these resinous bodies, under such conditions that they could be used for definite technical purposes.

When in 1891 formaldehyde had become a relatively inexpensive article of commerce, Kleeberg⁴ took up this matter anew, and found that by bringing together a mixture of formaldehyde solution, phenol and hydrochloric acid, a violent reaction ensues,

¹ See Wohl, *Ber.*, **19**, 1892. Tollens, *Ber.*, **17**, 653. Carl Goldschmidt, page 29. Bonn, Verlag von Friedrich Cohn, 1903.

² See Cambier, Brochet, *Compt. rend.*, **120**, 557.

³ *Ber.*, **5**, 1095; **19**, 3004 and 3009; **25**, 3477; **27**, 2411.

⁴ *Ann.*, **263**, 283.

and the whole mass changes to an amorphous, hard, resinous body, of irregular shape, a mixture of various heterogeneous substances, including remnants of the reacting materials. He was confronted by the fact that trying to purify this substance, or to establish a constant composition, was a rather thankless job, especially so as the biggest part is insoluble and not amenable to the usual methods of purification; after giving a limited attention to this subject, he pursued his work along the line of other condensation products, which can be obtained in crystalline form.

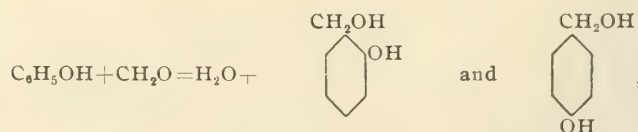
Afterwards, various attempts were made by Smith, Luft, Blumer, Story, DeLaire and others, to try to modify this reaction, so as to produce more definite bodies than those obtained by Kleeberg.¹ Their efforts were directed towards moderating the reaction by limiting the temperatures, or by diluting the reacting materials in suitable solvents. It was thus found that, according to circumstances, resins could be obtained which are soluble in alcohol and similar solvents, and which can be heated and melted, and which under treatment of heat remain indefinitely fusible, and behave much like shellac or similar natural resins. For that reason, they are called shellac-substitutes, and I have published a special paper on this subject,² in which I designate these artificial soluble and fusible resins, under the general name of Novolak.

Under other conditions, entirely different bodies are obtained which, although resinous in appearance, can no longer be considered as true resins, and lack the chemical characteristics of resins. They are infusible and insoluble. However, the preparation of these infusible substances involved several objectionable conditions, which made them of little, if any, practical value. All this is described in my former publications on this subject.³

I undertook a systematic study to establish the chemical constitution and the relation which exists between these infusible bodies, the fusible, soluble, resinous condensation products, and the substances from which they are derived. I was able to dissect this perplexing reaction in several distinct transition stages, which can be produced at will. It seemed at first that the formation of these very dissembling bodies was simply a matter of relative proportions of reacting materials, or of quantity of condensing agents, but I became convinced that this is not so simple and that the reaction involved several, until then unobserved or neglected, phenomena which have a paramount bearing on the results.

By conducting the process in several stages, and more particularly by effecting the synthesis from different starting points, I succeeded in gaining enough insight into the problem that I could devise some sure practical methods for obtaining new results. Since then, several years of uninterrupted hard work have enabled me to devise various technical applications, with most of which you are already acquainted. One of my first problems was to determine why

different experimenters had obtained such dissimilar results when starting from almost identical products. For instance, Lederer¹ and Manasse² by acting with one molecule of CH_2O on one molecule of $\text{C}_6\text{H}_5\text{OH}$, in presence of one molecule of NaOH , then acidulating, obtained ortho- and paraoxybenzylalcohol,



which is a nicely crystalline, water-soluble body, known also as saligenin, very different from the resinous amorphous condensation products. Saligenin had formerly been prepared from its glucoside, salicin, which was extracted from the willow tree.

Then again, DeLaire,³ operating under rather similar conditions, using about the same proportions of alkali, phenol and formaldehyde, then acidulating, and heating afterwards, obtained fusible soluble resins of totally different character than oxybenzylalcohol. These resins are identical with the soluble fusible resins which he and others obtained by heating directly acids with a mixture of formaldehyde and phenols, but they are totally different from the infusible, insoluble mass Kleeberg and others obtained by heating hydrochloric acid with the same mixture of phenol and formaldehyde. At that time, those results seemed rather irreconcilable with each other, and it very often happened that two operators, starting from the same mixtures, obtained totally different products by simply changing somewhat their way of working. Some workers in this line seemed to pin their faith to the fusible, soluble resins, or Novolak, and used every means to exclude the disturbing insoluble bodies which tended to form. Others again tried to utilize the infusible bodies. It soon became evident to me that the bodies of the latter kind prepared up till then had not attained their full best qualities because they were produced at too low a temperature in presence of acids and in admixture with solvents or with an excess of phenol.

I found that decidedly higher temperatures than those preconised for these products were very desirable, not only for improving the end product but more especially for insuring rapid formation and rapid molding. But when I tried to employ high temperatures, I was immediately confronted, like my predecessors, with the same difficulties; namely, high temperatures bring about violent uncontrollable reactions, accompanied with self-heating and with the evolution of gaseous products, which render the mass porous. This was the very reason why those who had preceded me had carefully recommended in all their descriptions, not to use temperatures exceeding 50 to 80° C., or at the utmost, 100° C.; even then, they were compelled to use solvents or,

¹ See Baekeland, *THIS JOURNAL*, 1, No. 3, March, 1909, published by the American Chemical Society, Easton, Pa.

² See Baekeland, *THIS JOURNAL*, 1, No. 8, August, 1909.

³ See Baekeland, *Ibid.*, 1, No. 3, March, 1909, 1, No. 8, August, 1909.

¹ *J. prakt. Chem.*, [2] 50, 224.

² *Ber.*, 1984, 2409-11; D. R. P., Baeyer, 85,588; U. S. P., Manasse, 526,786, 1894.

³ French Patent, No. 361,539.

in some cases, an excess of phenolic body so as to moderate the reaction by these diluents.

I became aware of the fact that the disturbing emission of gaseous products, whenever the reaction is carried out at too high a temperature, has the characteristics of chemical dissociation. Its disturbing action could be moderated by introducing a solvent, for instance, an excess of phenol, in which the gaseous products could provisionally accumulate until they established a dissociation equilibrium. But I concluded that the easiest and most practical way to prevent gaseous dissociation, and the resulting porosity of the mass, was to exert a suitable counter-pressure. This allows us to use as high a temperature as we may desire, by increasing the counter-pressure accordingly. This can be done in several ways, either by heating in a closed vessel in which the pressure raises by itself, or better in a vessel in which air or another gas is pumped, under pressure, before the heating begins. One of the most practical ways, and specially suitable for molding, is the use of a heated hydraulic press.

Permit me to say here that before I took up this subject, no other methods for molding infusible condensation products of phenols and formaldehyde had been suggested than so-called cast-molding, consisting in pouring the original mass in a mold and heating moderately without pressure until solidification sets in.

The technical problem was advanced further by utilizing the following observation:

If formaldehyde and phenols are heated in presence of an acid condensing agent, an insoluble body *may* or *may not* be the result. This does not depend on the amount of acid nor whether the reaction is allowed to proceed violently, or slowly; neither does it depend on the amount of formaldehyde which has been used; but it all depends on the amount of formaldehyde which has really entered into reaction. For instance, if the reaction be carried out in presence of an acid condensing agent, with an amount of phenol exceeding 15 molecules of phenol for 14 molecules of formaldehyde, a fusible, soluble resin of the Novolak type is most likely to form. The same thing occurs even if large amounts of formaldehyde are used, but if for some reason or another, enough formaldehyde is volatilized, or otherwise lost during the reaction.

I found that these uncertainties do not exist if, instead of an acid condensing agent, we use a small amount of a base. Bases had been used before but in much larger proportions, by which they form substances entirely different from those I have in view. Relatively small amounts of ammonia, alkalies, amines or other basic substances, added to a mixture of phenols and formaldehyde, enabled me in every case, after heating, to produce insoluble, infusible end products, regardless whether the amount of phenol is or is not in excess. With the use of small amounts of basic condensing agents, there is no longer any doubt as to the result, and the reaction becomes so easy to control as to lend itself to the

most varied industrial applications. By the use of bases the initial reaction can easily be interrupted at will, so as to obtain stable intermediate products, which simplify the whole process so as to make it a practical industrial operation. Furthermore, the presence of these small quantities of bases in the initial condensation product accelerates, at relatively low temperatures, the final hardening by polymerization. This beneficial accelerating action is so pronounced that, with some precautions, the process of hardening can be carried out in a much shorter time, and without the use of any counterpressure; for instance, by starting at relatively moderate temperatures, say about 80° C., and as soon as the mass begins to harden by raising the temperature with increasing rapidity to 110° C. and over. For very thin layers, this precaution of gradual heating can even be omitted, and the maximum temperature can be applied at once, without any danger of blisters or porosity.

However, in most cases it is decidedly more practical to heat directly at maximum temperature, under suitably increased pressure. In this way, hardening and moulding can be accomplished in as short a time as one to five minutes, according to the thickness or the size of the object. My published patents contain a description of these processes, and I shall limit myself to the following brief description:

About molecular proportions of phenol and formaldehyde are boiled in presence of suitable amounts of ammonia, or sodium hydroxide. This gives an initial product which is called A, and which can be purchased in the trade either in liquid, or in solid condition. A is the immediate and first result of the condensation reaction, whereby formaldehyde in reacting upon phenol increases the carbon nucleus of its molecule, this phenomenon being accompanied by a corresponding chemical elimination of water. This A, our initial condensation product, is soluble in alcohol, acetone and similar solvents. Certain varieties of A can be kept indefinitely, or at least for a long time, without alteration. A is characterized by the very distinct property that when it is further heated, it will ultimately be transformed into a final infusible, insoluble substance, of great hardness, called Bakelite "C," and this is the final product at which we aim in the whole process.

Solid A, on account of its physical appearance and its solubility in alcohol or acetone, might easily be mistaken for one of the permanently fusible, soluble resins of the Novolak type. But such a mistake is impossible if we bear in mind that Solid A, when heated, although it may melt for awhile, soon becomes hard, infusible and insoluble by polymerization. Novolak, on the contrary, if heated, simply melts and sets again by cooling, but it does not harden to an infusible, insoluble body by simple application of heat.

In my former publications¹ I have described also an intermediate product, B, the existence of which is of considerable importance for certain industrial

¹ Backeland, *loc. cit.*

applications, because, although being infusible and insoluble, it nevertheless, possesses the property of softening if heated, and of welding and molding under the combined action of heat and pressure.

There are several other ways of obtaining "C," for instance, Lebach (Knoll & Co.) uses a base as a condensing agent, and mixes the so obtained "A" with a strong acid, and heats at a moderate temperature.¹

"C" can also be produced by heating oxybenzyl alcohol with CH_2O , or its equivalents.² Or instead of starting from oxybenzyl alcohol, we may start from Novolak, and heat it with CH_2O , or equivalent substances.³ DeLaire⁴ has already shown that the fusible soluble resins are anhydrides of phenol alcohols. This can easily be demonstrated by heating, preferably *in vacuo*, oxybenzyl alcohol in a test tube at 160-170° C. Heating oxybenzyl alcohol, in presence of acid solutions, favors considerably the formation of these anhydrides, or saliretins, saligenosaligenin, and similar products.⁵ I believe this explains to us why bodies of the Novolak type are more easily engendered in presence of acid condensing agents, provided the CH_2O be not used in excess.

The intervention of condensing agents for the formation of fusible, soluble resins of the Novolak type is not indispensable. This has been shown as far back as 1905 by Story,⁶ who, by simply boiling an excess of phenol with formaldehyde *without any condensing agent*, and evaporating afterwards, has obtained a soluble, fusible resin of the Novolak type. Lately, Aylsworth⁷ has confirmed this method in a somewhat more complicated way. All these fusible resins are simply anhydrides of the corresponding phenol alcohols. Their fusibility and solubility are augmented by the presence of small amounts of phenolic bodies. In my former publication "On Fusible, Soluble Resinous Condensation Products of Phenols and Formaldehyde,"⁸ I considered these bodies as definite compounds of saliretin products, with a small excess of phenol. More recent work on the same subject, the details of which are not yet ready for publication, compels me to abandon this interpretation. We have to deal here simply with physical mixtures, in the form of colloidal solid solutions of saliretin products with very small quantities of phenols. These small amounts of phenol are retained stubbornly by the phenol alcohol anhydrides or saliretin products forming therewith a solid solution; this accounts for the difficulty of their complete removal.

This makes the chemistry of this whole subject

¹ See U. S. P., Lebach, 965,823.

² See Baekeland, *THIS JOURNAL*, **1**, No. 3, March, 1909.

³ See Baekeland, "On Soluble, Fusible, Resinous Condensation Products of Phenols and Formaldehyde," *THIS JOURNAL*, **1**, No. 8, Aug., 1909; Belgian Pat., 213,576, February 15, 1909.

⁴ See British Patent, 15,517, 1905.

⁵ Beilstein, *Organ. Chemie*, **2**, 1109 (1896). R. Piria, *Ann. Chem.*, **48**, 75; **56**, 37; **81**, 245; **96**, 357. *Motessier Jahresbericht*, **1886**, 676; K. Kraut, *Ann. Chem.*, **156**, 123. Gerhardt, *Ann. Chim. Phys.*, [3] **7**, 215. F. Beilstein and F. Seelheim, *Ann. Chem.*, **117**, 83. C. Schotten, *Ber.*, **1878**, 784.

⁶ D. R. P., 308,449.

⁷ Belgian Patent, 232,899.

⁸ *THIS JOURNAL*, **1**, No. 8, August, 1909.

extremely simple. The fusible, soluble resins of the Novolak type are merely the old known saligeno saligenins, saliretins, or anhydrides of phenol alcohols, containing in some cases, in solid solution, a smaller or larger amount of phenols.

If then we take into consideration that I succeeded in making C by heating six molecules of oxybenzyl alcohol with at least one molecule CH_2O or its equivalent, and that the same result is attained by heating Novolak or other anhydrides of phenol alcohols with the required amount of formaldehyde, the explanation of a heretofore rather perplexing set of reactions becomes exceedingly simple.

Instead of directly preparing Solid A by starting with phenol and formaldehyde and a base, we can make it in two steps: first, prepare Novolak or any other saliretin products and then melt and mix it with the polymers of formaldehyde, and thus obtain a variety of Solid A, practically identical to the Solid A obtained by direct action of phenol and formaldehyde in presence of a base. This Solid A, by further action of heat, will then change into hard infusible, insoluble "C."

The similarity of the Solid A thus prepared is even greater if, instead of using formaldehyde, we use a mixture of formaldehyde and ammonia, so as to accelerate the hardening process. In place of this mixture of formaldehyde and ammonia, we can use its preformed and direct equivalent, hexamethylenetetramin. However, in the latter case the amount of ammonia introduced into the mixture, with the required amounts of CH_2 group, becomes much larger than strictly necessary, and on account of this as soon as the final hardening sets in this excess of ammonia is liberated.

If the temperature of such a hexamethylenetetramin mixture be raised above 110° C., self-heating starts in, and the whole mass raises like a sponge, while hardening: this on account of the sudden liberation of ammonia vapors. This phenomenon which I show you here is in direct contradiction with the statement of Mr. Aylsworth.¹ It is quite true that my method of using counterpressure in a hydraulic press, or otherwise, can easily be called into service here, so as to allow the use of the high temperature at which rapid molding and hardening becomes possible. In this respect, small amounts of fixed alkalies, like caustic soda, have decided advantages over ammonia, or hexamethylenetetramin, in as far as they do not exaggerate the tendency of forming gaseous products by the elimination of NH_3 , which causes foaming and porosity during the application of heat in the hardening process.

The properties of Bakelite, its chemical constitution, and some of its industrial applications, have been so often described that I will dispense with a general repetition thereof. The fact that it only chars at relatively high temperatures, its infusibility, its hardness, and tenacity, its resistance to physical and to most chemical agents, and its ease of manipulation explain sufficiently its uses in the arts.

¹ See Belgian Patent, Aylsworth, 232,899, February 11, 1910.

In my former publication on the subject, I have insisted, in order to better differentiate its properties from those of hard rubber and celluloid, that it lacks the flexibility of the two latter products, but I have found since then that my statements have been taken too absolutely, instead of in a comparative sense. Here is, for instance, a thin plate of Bakelite, which is flexible enough for many purposes, and which is, furthermore, quite strong, but you will notice that if I bend it in an exaggerated manner it suddenly will snap off and break in many small pieces. It resembles in this respect a thin plate of glass, but it is not so fragile and is more flexible. Thrown on a hard surface, it will not break as easily as glass and will rebound. Nevertheless, it cannot stand the seemingly endless bending of the very flexible varieties of celluloid. There is no difficulty whatever, by the introduction of some substances which produce colloidal solid solutions, to make Bakelite so soft and flexible that a rod thereof can be twisted around one's finger; but in introducing these extra matters, many of the other excellent qualities of Bakelite are sacrificed to a considerable extent; for those applications where great flexibility is required, rubber and celluloid answer, incomparably better, the purpose.

I found that we can enormously increase the practical uses of Bakelite by incorporating it with structural fillers, like fibrous or cellular bodies. The beneficial action of the latter is remarkable, and seems to consist mainly in modifying the shattering wave which develops whenever an object made of Bakelite is submitted to a violent shock. Some substances, like rubber or celluloid, are weakened if they are mixed with large amounts of fibrous materials. But Bakelite is strengthened by fibrous materials, on account of its low flexibility and other specific properties, probably also by the fact that its fusible parent "A" impregnates homogeneously any fibrous or cellular materials with which it is incorporated, instead of remaining on the surface like rubber or celluloid. It produces, with fibrous fillers, compositions which are strikingly much stronger and less breakable than if it be used alone or in conjunction with structureless fillers. This valuable property has been put to excellent advantage in the manufacture of many molded and impregnated articles where Bakelite is used in smaller proportions as a binder for fibrous bodies. This is best illustrated by some of the molded solid buttons, insulators, phonograph records, brush-backs, magneto distributors, knife-handles, pressed plates, and other manufactured objects you see here before you, many of which have been molded in the hot hydraulic press, without any after-treatment. Some of these articles have been molded and finished in a few minutes' time; others of large size require some longer heating.

Here is a third rail insulator block, molded from a mixture of asbestos fiber and Bakelite. From its excellent appearance, you would never imagine that it has had two years of strenuous service for heavy passenger traffic on the third rail system of the New York Central lines, exposed to rain and

sun and all the extreme conditions of our variable climate.

Molded compositions of ordinary asbestos and Bakelite, containing less than one-third of Bakelite, have shown on the Riehle testing machine tensile strengths as high as 4490 lbs. per square inch, and by selecting carefully the fibrous material still better results can be obtained.

The following electric tests will give a general idea of the dielectric value of Bakelite and some of its composition:

Composition. * Different varieties of transparent "C" made specially for electrical purposes by hardening liquid "A" on a glass plate in a stove:	Thickness testing piece in millimeters.	Volts per millimeter at puncture. Tested with a 50 kilowatt transformer, raising voltage gradually so that puncture occurs within 20 to 30 seconds.	
		Punctured at	
Sample 1.....	1.78		17,400
Sample 2.....	2.18		14,200
Sample 3.....	2.60		13,400
Sample 4.....	0.43	16,750	38,800
Sample 5.....	0.9	23,300	28,000
Sample 6.....	0.95	25,600	26,900
Molded composition:			
70 Asbestos.....	8		
30 Bakelite.....	8		8,500
Molded composition wood flour and Bakelite....	7.9		11,000
Impregnated blotting paper, hardened in a hot hydraulic press....	3.66	102,000	27,880
Pressed paper impregnated with Bakelite...	1.6	53,700	33,500

Some other tests (Electrical Testing Laboratories of N. Y.) have shown an unusually high specific inductive capacity, which makes the material very suitable for electrical condensers.

Pressed paper, impregnated with Bakelite, has been recommended in Germany for the manufacture of electrostatic machines. Its value for this purpose may reside in the fact that it withstands rather well the action of ozone, which is not the case with resins, or with hard rubber. In fact, hard rubber is known to coat itself by and by with an extremely thin film of sulphuric acid, due to slow oxidation of the sulphur. This sulphuric layer, although microscopically thin, causes considerable disturbances for some electrical applications. The impregnation of electric coils with Bakelite is now regularly practised on an industrial scale by several electric manufacturing companies. Its advantages for this purpose are obvious on account of the fact that in case of an increase of temperature, through overload or otherwise, the impregnating material cannot melt; but there is another important factor, namely, this substance, notwithstanding its good electric insulating properties, is a better conductor of heat than the resinous materials or varnishes generally used for the impregnation of dynamos or motors, so that the generated heat is better conveyed to the outside. At any rate, it has been observed that coils impregnated with Bakelite heat up much less than others impregnated with resinous bodies.

Bakelite has rendered excellent service as a glue;

one of its latest applications on a commercial scale is shown by these brushes, of which the bristles are held together with this binding material, which is indifferent to any of the solvents used in paints, varnishes, paint removers and to soap or hot water. It is cheaper and easier to apply than rubber, which has lately been used extensively in the United States for the same purpose. Furthermore, the hardening can be conducted at temperatures so low that white bristles are not discolored.

Let me draw also your attention to these samples of fancy articles, like cigar holders and pipe stems, made of "C," perfectly transparent. Some have the color of amber; others are as colorless as glass. You will notice that they are entirely devoid of odor or taste, even if you rub them. If I insist on this point, it is merely to eliminate an erroneous impression, which has gained some ground, that Bakelite has a particular smell. If there was any smell at all, it would only show that the transformation in C had not yet been complete.

As chemists, you are undoubtedly more interested in the application of Bakelite for laboratory work, or for chemical engineering purposes. Time forbids me to take up the subject in detail. But I may state that a dilute alcoholic solution of "A" finds many uses in the laboratory. Dipping or spraying of metallic objects in or with a solution of the kind, followed by treating in a stove at a temperature of about 120° C. or above, provides them rapidly with a hard protective coating. The time of hardening varies from one minute to half an hour or more, according to the available temperature. If blisters are caused, this indicates that the solution is too thick. This gives us a very economical means for transforming an ordinary sheet-iron-kitchen-gas-oven, which can be purchased at any hardware store for one to two dollars, into a very efficient substitute for the expensive copper drying stove.

Leaks or cracks in glass apparatus can easily be made tight by the skilful application of this solution. In certain cases, asbestos paper or tape, used in conjunction with varnish or Liquid A, will prove an excellent reinforcement.

There is a special variety of Liquid A, which can easily be mixed with asbestos fiber, or clay, or silex powder or baryta, so as to make a very soft dough-like-mass.

If I apply this soft mass to a hot steam pipe, it will stiffen rapidly, until it becomes as hard as stone. By the fact that it contains a base hardening agent, the hardening can take place easily at temperatures as low as 75° C., although higher temperatures will give quicker results. This makes an excellent mixture for spreading on the surface of cast iron pipes or other parts of machinery which have to be protected against the corrosive action of some chemicals. Here is, for instance, a part of an iron casting, the inside of which has thus been protected by applying this paste as a 1/4-inch inside lining. These protected iron castings have been used in a large electrolytic plant, where they have been submitted for more than a

year, day and night, continuously to contact with rapidly moving hot brine and hot chlorine, at temperatures of about 70° C. For such purposes it is always better to apply the material abundantly, because it is very difficult to spread a thin film of any material so uniformly that there should not exist some unprotected places where corrosion can occur.

For certain chemical uses like digesters, the possibility of chemical corrosion is augmented by mechanical abrasion, due to the friction of moving liquids or solids. For such purposes, there exists a simple and efficient way for lining the vessel with acid-proof bricks, held together with Bakelite cement. This is accomplished in a somewhat similar way as porcelain-lined ball mills are made, with that difference that the walls of the vessel ought to be first lined with a thin sheet of asbestos paper, impregnated with liquid A; on this the brick lining is inserted and fastened with liquid A or better with a cement made with liquid A and some inert filling materials, like clay, baryta, or powdered silex, or asbestos. This liquid mixture is easily applied, and then a suitable heater, for instance a gas-stove, is introduced in the vessel, so as to raise the temperature of the lining to at least 80° C., or higher, until the polymerization into C has taken place.

Whenever asbestos is used as a filling material, it should not be forgotten that Canadian asbestos is easily attacked by acids. Amphibole asbestos is considerably more resistant to acids; unfortunately, it lacks strength and fibrous qualities. Green Cape asbestos resists acids well and has a good strong fiber, but is more expensive.

THE "KAISER WILHELM INSTITUT FUER PHYSIKALISCHE CHEMIE UND ELEKTROCHEMIE" IN DAHLEM NEAR BERLIN.

By WILLIAM D. HARKINS.

Received October 4, 1911.

On October 1st Professor F. Haber began his work as Director of the new Kaiser-Wilhelm Institute für physikalische Chemie und Elektrochemie at Dahlem near Berlin. The buildings of the Institute, work upon which was begun during the present summer, are being erected by the Prussian government working in conjunction with the "Koppel-Stiftung" for the purpose of improving the intellectual relations of Germany with other lands."

The "Koppel-Stiftung" which was founded in Berlin some years ago by Geheimer Kommerzienrat Leopold Koppel, and which until now has maintained the German School of Medicine in Shanghai and the American Institute in Berlin, will provide the funds for the erection of the new Institute and will also give thirty-five thousand marks annually for its maintenance during a period of ten years. The Prussian government has provided the site which is situated at the terminus of the new underground railway from the center of Berlin to Dahlem, and

has endowed the Institute with the sum of fifty thousand marks annually.

The Institute will be controlled by a board consisting of two representatives of the German government, two representatives of the Koppel-Stiftung, and the Director of the Institute. The Director has an absolutely free hand in the choice of his work, his fellow workers, and his assistants.

For the admission of investigators who wish to follow their own lines of investigation in the Institute with their own means, the Director must have the assent of the board of control.

The Institute will consist of scientific and technical departments in separate buildings. The building of the scientific department is 600 square meters in ground area, and has a basement entirely underground containing constant temperature rooms. On the ground floor are the professor's laboratory and

the machinery hall with a floor space of two hundred square meters. This hall is surrounded by smaller rooms for chemical preparations, high voltage and heavy current work, and a blacksmith shop. The ground floor of the technical building contains a consultation room and the laboratory of the assistant in charge of that department. On the first floor are the living accommodations for two assistants and an engine-man, and also a room for the serving of refreshments.

The Director's house will be erected in the grounds of the Institute.

Although there exists no stipulation on the point, it may be taken as a rule that, on account of the fact that no teaching as such is to be undertaken, only such students will be admitted by the Director as have already finished their normal university course and desire a wider experience in scientific research. This will mean



PROFESSOR HABER AND STAFF AT KARLSRUHE, 1911.

consulting room, the offices, the calibrating room in which are to be kept the necessary laboratory standards, the mechanic's shop, and a lecture theatre to seat twenty-five persons. Further lecture rooms are not provided in the building as *teaching in the ordinary sense is not contemplated in the Institute*. The first floor will be devoted to the library, chief assistant's room, glass-blowing room, and a laboratory for eight research men. On the second floor are the living rooms for the mechanic and his family, since the mechanic also acts as caretaker. This floor also contains rooms for photochemistry, for scientific collections, and work places for several more research workers.

The building is connected by a corridor with the technical department whose important feature is

that students who come directly from American universities should have the degree of Doctor of Philosophy in Chemistry, or Physics, or an equivalent training. There are no restrictions whatever as to the nationality of the men admitted by the Director.

The Director of the Institute, Professor Haber, was born in Breslau in 1868, and obtained his Ph.D. in Berlin in 1891. After obtaining his degree he spent several years, partly in technical work and partly in securing further scientific training. In 1894 he went to Karlsruhe and was appointed Privat-dozent in Chemical Technology in 1896, and ausserordentlicher Professor in 1898. In 1902 he was sent to America by the Bunsen Society of Applied Physical Chemistry to study the system of chemical instruction and the condition of electrochemical industries in

the United States. In 1906 he was appointed to the post of ordentlicher Professor in Physical and Electrochemistry in Karlsruhe, where he built up the best equipped research laboratory of Physical Chemistry in the world. Students from all parts of the world were attracted to this laboratory to such an extent that its accommodations were insufficient to allow all of them to enter, even although Professor Haber admitted as many as forty men at one time as research workers. What was most remarkable was that he personally directed the work of all these men, and often aided them in their experimental work. In 1907 he was called to take the place of Lunge in Zurich as professor of chemical technology, and in 1909 he was asked to undertake the control of one of the largest chemical works in Germany, but he declined both of these appointments.

Professor Haber introduced into Germany the rational method of instruction in elementary chemistry as embodied in the laboratory outline written by Alexander Smith. This book was translated into German by Professor Haber and Fritz Hiller.

The two books, 1898 *Lehrbuch der technischen Elektrochemie auf wissenschaftlicher Grundlage* (now out of print), 1905 *Thermodynamik technischer Gasreaktionen* (English edition 1908), together with numerous contributions to the *Zeitschrift fuer Elektrochemie*, *Wiedemann's Annalen*, and the *Zeitschrift fuer physikalische Chemie*, constitute his literary activities.

One of Professor Haber's most important researches was that upon the ammonia gas equilibrium at high

temperatures. This work resulted in the development of a commercial method for the manufacture of pure ammonia directly from the elements by the use of osmium or uranium as a catalyzer. Another important series of researches was that upon the properties of flames, including the gas equilibria involved, the ionization and conductivity of the gases, and the action of the ions as catalyzers. He has spent much time during the last few years upon the study of the escape of electrons from the reacting surfaces of metals, and the effects of electrons upon gas equilibria and upon the velocity of chemical reactions. His other recent researches have been mostly upon the following subjects: the electromotive force of the oxyhydrogen cell at high temperatures; the oxidation of nitrogen in the high potential arc; a gas refractometer for the optical analysis of gases; according to Rayleigh's principle, electrical forces at phase boundaries; the corrosion of iron by stray currents from street railways; the reduction of hydroxylamine; the use of solid materials such as glass and porcelain as electrolytes; the equilibrium between magnesium chloride and oxygen; electrode potentials and electrolytic reduction; the laboratory preparation of aluminium; the preparation of hydrogen peroxide by electrolysis; experiments on the decompositions and combustion of the hydrocarbons; and autoxidation.

The writer wishes to thank Dr. Fritz Hiller, of Berlin, for the greater part of the information contained in this article. The statements in regard to the purposes and government of the Institute are official.

UNIVERSITY OF MONTANA,
MISSOULA

SCIENTIFIC SOCIETIES

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.

The Annual Meeting of the Institute will take place in Washington, December 20th to 23d, with headquarters at the New Willard Hotel. After the regular business sessions and reports of committees, the following program will be presented:

PROGRAM

NEW WILLARD HOTEL, WEDNESDAY, DECEMBER 20TH.
9.30 A.M.

Address of welcome

Business session

Report of committees.

The following papers will be presented:

"Advances in Testing Explosives," Clarence Hall.

"Distribution of Power in Portland Cement Manufacture," Richard K. Meade.

"Manufacture of C. P. Acids," J. T. Baker.

"Manufacture of Gelatin," Ludwig Thiele.

"The Natural Bituminous Rocks of the United States," S. F. Peckham.

EXCURSION, 1.30 P.M.

Visit to Bureau of Standards:

The members of the Institute and their guests will be divided into three parties, making the following inspections:

(1) Inspection of adjustment of pyrometers, thermometers, pressure gauges and similar instruments.

(2) Inspection of the standardizing of weights and measures.

(3) Inspection of liquid air apparatus to be in operation for the benefit of the visitors.

MEETING, 8.00 P.M.

Address of the Retiring President, Dr. F. W. Frerichs.

(a) "Manufacture of Chloroform from Alcohol."

(b) "Manufacture and Testing of Shipping Cylinders for Liquid Ammonia with the Design of Valve."

"The Manufacture and Testing of Carbonic Acid Cylinders," John C. Minor, Jr.

THURSDAY, DECEMBER 21ST.

EXCURSION.

U. S. Proving Grounds at Indian Head.

(Notice should be given to the Secretary immedi-

ately, stating nativity, citizenship and business connection, by those who desire to make this visit, as same must be submitted for approval.)

The Proving Grounds comprise plants for contact sulphuric, nitric and mixed acids, the nitration of cellulose and recovery drying; powder presses, mines and heavy artillery.

DINNER IN NEW WILLARD HOTEL, 7.00.

FRIDAY, DECEMBER 22ND, 9.30 A.M.

Installation of officers.

Business session.

SYMPOSIUM ON THE UNITED STATES PATENT SYSTEM.

"The United States Patent Office," by E. B. Moore, Commissioner of Patents.

"Patent Office Procedure" (Practice of Patent Law up to the issue of the Patent), Edward T. Fenwick, of Mason, Fenwick and Lawrence.

"Protection of Inventions by Patents: Existing Defects and Remedies Therefor," by W. D. Edmunds, of Edmunds and Peck.

"Patent Litigation," by R. N. Kenyon, of Kenyon and Kenyon.

2.30 P.M.

Reception at the White House.

The President will receive the members of the Institute in the East Room of the White House.

3.00 P.M.

Visit to the Patent Office.

8.00 P.M.

"The Adaptation of the Centrifugal Pump to Chemical Service," (illustrated with lantern slides), by F. G. Wheeler.

Business session.

SATURDAY, DECEMBER 23D, 9.30 A.M.

Excursion (alternative):

(a) Steel Plant at Sparrows Point, Baltimore.

(b) Cement Plant of Tidewater Portland Cement Co.

Association of American Portland Cement Manufacturers. Dec. 11-13. Annual meeting at New York City. Secy., Percy H. Wilson, Land Title Bldg., Philadelphia, Pa.

American Society of Agricultural Engineers. Dec. 27-29. Annual meeting at St. Paul, Minn. Secy., J. B. Davidson, Ames, Iowa.

NOTES AND CORRESPONDENCE.

MANGANESE IN STEEL.

To the Editor of the Journal of Industrial and Engineering Chemistry:

As a suggestion to those using Walter's persulfate method for manganese in steel, the writer has found that by using 10 cc. of a 15 per cent. aqueous solution of ammonia persulfate instead of adding the dry salt to the HNO_3 solution of the steel in the test tube, the tendency to foam and the color to fade is overcome, and a much clearer solution results. Also 5 cc. of a AgNO_3 solution containing 4 grams per liter are used instead of the usual 15 cc. containing 1.33 grams per liter. This keeps the volume of the solution below 30 cc.

This method also gives good results by titration with sodium arsenite, the only difficulty being a yellowish brown tinge toward the end of the reaction, making the end point rather hard to distinguish without a great deal of practice. The writer is now at work trying to find a way of obviating this difficulty, making the end reaction sharp and distinct.

PITTSBURG, CALIFORNIA,
November 2, 1911.

GORDON L. VON PLANCK.

ELECTROLYTIC "ALTERATIVE."

To the Editor of the Journal of Industrial and Engineering Chemistry:

Now that so much work has been done to render

the copper electrolytic process more efficient by the addition of various substances to the electrolyte it seems regrettable that no more appropriate title than that of "addition agents" has come into use. In this connection the word "alterative" seems to be somewhat more suitable, or to be more explicit, "electrolytic alterative."

J. L. HACKETT.

FLUSHING, N. Y.,
October 27, 1911.

WESTERN PHOSPHATE DEPOSITS.

Until recently it had been generally assumed that the phosphate deposits of South Carolina, Florida, and Tennessee afforded an "inexhaustible" supply, but recent estimates by the Geological Survey show that at the present rate of increase in phosphate mining these eastern deposits are likely to be exhausted within a generation.

The discovery of the western phosphate beds, therefore, constituted a most important find, and though the first reconnaissance of these deposits by the Geological Survey showed their considerable extent, the more detailed study and exploration, with additional discoveries made by the Survey during the last three years, have shown that the field is probably the greatest in the world. Recent geological study of the phosphate-bearing strata indicate the probably still greater extension of the phosphate

area. The northernmost portion of the beds first discovered was in Wyoming, but an outcrop of the same character and in the same geologic formation was found last year in Montana, some 160 miles farther north, so that Survey geologists believe that workable phosphate beds may be found in many other places.

The Geological Survey has just published a bulletin embracing three reports on western phosphate fields, one covering a portion of the Idaho phosphate reserve, by R. W. Richards and G. R. Mansfield, another on rock phosphate near Melrose, Mont., by Hoyt S. Gale, and a third being a reconnaissance report on the phosphate deposits in western Montana, by Eliot Blackwelder. The report by Messrs. Richards and Mansfield includes a detailed description of the Idaho field, the investigations having been made by townships, the outcrops examined, and the tonnage of high-grade phosphate rock estimated. Tonnage estimates were made of the phosphate rock in nine townships, and in no township was there found to be less than approximately 60,000,000 tons of high-grade phosphate rock, containing for the most part from 50 to 82 per cent. phosphoric acid.

One of the townships examined contains an estimated 293,000,000 tons of phosphate rock, the net result of the Survey's work showing an approximate tonnage of 2,500,000,000 long tons with 70 per cent. phosphoric acid. Nor does this include the tonnage of the Montana phosphate withdrawals, which aggregate nearly 34,000 acres.

Mr. Gale's report is a brief description of his discovery last year of the Montana deposits near Melrose, withdrawals of which were immediately made by the President. The Survey's tests of a number of samples collected by Mr. Gale show the rock to be high-grade, approximately equivalent to 75 per cent. phosphoric acid. The thickest beds are 6 or 8 feet in thickness. A 6-foot bed would contain approximately 21,000 long tons to the acre.

"One of the most important considerations in connection with the discovery of phosphate rock in western Montana," says Mr. Gale, "is its significance as to the probable extent of the western phosphate fields, for it now appears probable that similar deposits may extend over a large part of western Montana. Their nearness to the large copper smelters is important, for these smelters produce great quantities of sulphuric acid and sulphurous acid fumes which are usually allowed to go to waste through the smoke-stack of the plant. Reduction of phosphate rock by means of sulphuric acid appears to offer what is perhaps the largest commercial use for these waste products of the smelters." Mr. Gale quotes a report showing the daily loss at the Anaconda smelter alone of about 3,800 tons of sulphuric acid.

Mr. Gale suggests a further innovation in the treatment of phosphate rock which would greatly reduce the transportation charges that at present stand in the way of development. By this process a ton of concentrated phosphate would equal three tons of ordinary superphosphate. The fertilizer distributor

would therefore pay freight on one ton where he now pays it on three.

The report calls attention to the fact that under the present mining law there appears to be no adequate provision for the disposal of phosphate lands, and that it is presumed that Congress will, in the near future, pass some well-considered measure to cover this need.

Mr. Blackwelder's contribution on phosphate in western Wyoming is a preliminary report and shows large and widely distributed deposits. He also mentions the presence of very great quantities of low-grade rock, which in course of time will doubtless be mined. For instance, in the Snake River canyon in western Wyoming he noted a total thickness of phosphatic beds exceeding 40 feet, of which about 29 feet contain more than 30 per cent. phosphoric acid and some beds contain 70 per cent. or more.

POTTERY PRODUCTION.

The manufacture of pottery of various kinds has grown to be an enormous industry in the United States, and it was in a highly prosperous condition in 1910, according to a report by Jefferson Middleton, United States Geological Survey. In 1899 the value of the pottery products of the United States was \$17,250,250. The product for 1910 was greater by \$16,534,420, a gain of 95.85 per cent. During the same period the imports increased 40.73 per cent.

The pottery products of the United States, as classified by Mr. Middleton, consist of red earthenware (flower pots); yellow and Rockingham ware (culinary utensils, teapots, etc.); cream-colored ware, white granite ware, semiporcelain and semivitreous ware, and china in its various forms (general household wares, such as table ware, toilet sets, etc.); sanitary ware (bathtubs, lavatories, washtubs, etc.); and miscellaneous wares, including art pottery made under various trade names, chemical pottery, jardinières, pins, stilts, and spurs for potters' use, porcelain door knobs, porcelain hardware trimmings, porcelain lighting appliances, smoking pipes, toy marbles, turpentine cups, umbrella stands, filter stones and tubes, and shuttle eyes and thread guides.

The product of most importance is white ware, which includes general household ware, though it is produced in only 8 states. This product was valued at \$14,780,980 in 1910, compared with \$13,728,316 in 1909. Ohio was the leading producer, reporting a value of \$9,730,408 for 1910. West Virginia was second and New Jersey third. White ware composed 43.75 per cent. of all pottery products.

Chinaware, the highest grade of general ware, though comparatively small in value of production (\$1,962,126 in 1910), showed a gain of \$195,306 in 1910. It was produced in but 3 States in that year. New Jersey was the leading State, reporting ware valued at \$1,131,412. New York was second and Pennsylvania third. China constituted 5.81 per cent. of all pottery products in 1910.

Sanitary ware was valued at \$6,758,996 in 1910, which was a gain of \$769,701 over 1909. It was produced in 9 States. New Jersey was by far the largest producer, the value of its output being \$4,955,066. West Virginia was second and Indiana third. Sanitary ware formed 20 per cent. of the value of all pottery products.

Porcelain electrical supplies were produced in 10 States in 1910, of which Ohio was the leader, reporting ware valued at \$1,277,144. These wares composed 11.23 per cent. of the total value of pottery products.

Red earthenware was made in 33 States to the value of \$854,196, Pennsylvania being the largest producer. Ohio was second and Massachusetts third.

Stoneware and yellow and Rockingham ware were valued at \$3,796,688 and were made in 28 States. This is the only branch of pottery production that showed a decrease in 1910. Ohio, as for many years, was the leading State in the manufacture of these wares, reporting 43.84 per cent. of the total. Illinois was second and Pennsylvania third.

Ohio is the leading pottery-producing State in the Union, reporting a value in 1910 of \$14,794,712, or 42.31 per cent. of the whole. New Jersey was second, with wares worth \$8,588,455, or 25.42 per cent. of the total. West Virginia was third, with wares valued at \$2,675,588. The 5 leading States—Ohio, New Jersey, West Virginia, Pennsylvania and New York—produced 88.60 per cent. of the total.

Imports of pottery in 1910 were valued at \$11,127,405, an increase of \$520,193, or 4.90 per cent. The exports of pottery, which are confined almost exclusively to the lower grades of ware, increased \$177,994, or 20.61 per cent. over the 1909 exports.

SAND-LIME BRICK.

The sand-lime brick industry was in a prosperous condition during the year 1910, according to statistics compiled by Jefferson Middleton, of the United States Geological Survey. These statistics also show a rapid development of the industry in recent years. The value of the production in 1910 was \$1,169,153, against \$1,150,580 in 1909 and only \$155,040 in 1903.

Michigan led in 1910, as for several years, and reported products valued at \$240,649; this was a gain of \$22,423, or 10.28 per cent., over 1909. Michigan's output constituted about one-fifth of the total value of all sand-lime products in 1910. Minnesota, the second in rank, producing \$154,250 worth, was the state to show the largest increase over 1909—\$41,181, or 36.42 per cent. New York was third in output, Florida fourth, and Pennsylvania fifth. Of the states for which totals are compiled by Mr. Middleton Indiana showed the largest proportional gain, 93.70 per cent. Of these States only two showed a decrease in value of the product, Iowa \$16,941, or 35.14 per cent.; and New York \$1,252, or 1.39 per cent.

EFFICIENCY OF SAND-LIME BRICKS.

The process of making sand-lime brick was in-

vented in Germany, where it probably has had its greatest development. Observations made there seem to prove that sand-lime brick is a building material which will resist shining soot. Three years ago an inn was built in Greifenhagen, in which sand-lime brick was used for everything but the lining of the chimney flues, which were built of common brick because at that time the question whether sand-lime brick was equally resistant to fire had not been settled. In spite of the fact that lignite briquets were burned, shining soot was found in the flues in a short time, and the flue bricks were permeated as high as the rafters of the ground floor. When the flues were pulled down it was found, however, that the sand-lime brick were entirely unharmed and white in color, in spite of the fact that the brick walls were only about 4½ inches thick. If this experience is repeated elsewhere, it is stated, the fact will be established that sand-lime brick is the best building material to withstand shining soot.

IRON AND STEEL INDUSTRY, 1910.

The iron and steel industry in the United States broke all previous records in 1910, according to Ernest F. Burchard, of the United States Geological Survey. The iron ore production was 56,889,734 long tons, the pig iron production 27,303,567 tons, and the steel production 26,094,919 tons. These figures show increases over the production in 1909 of iron ore 5,734,297 tons, pig iron 1,508,096 tons, steel 2,139,898 tons. The following table shows the enormous growth of the iron and steel industry in the United States since 1900:

	Iron ore.	Pig iron.	Steel.
1900.....	27,553,161	13,789,242	10,188,329
1905.....	42,526,133	22,992,380	20,023,947
1906.....	47,749,728	25,307,191	23,398,136
1907.....	51,720,619	25,781,361	23,362,594
1908.....	35,924,771	15,936,018	14,023,247
1909.....	51,155,437	25,795,471	23,955,021
1910.....	56,889,734	27,303,567	26,094,919

The value of the iron ore produced in 1910 was \$140,735,607, as against \$109,964,903 for 1909, and that of pig iron was \$425,115,235, as against \$419,175,000 in 1909.

Iron ore was mined in 28 States in 1910. The following table shows the production of the five leading States:

	Long tons.	Value.
Minnesota.....	31,966,769	\$78,462,560
Michigan.....	13,303,906	41,393,585
Alabama.....	4,801,275	6,083,722
New York.....	1,287,209	3,848,683
Wisconsin.....	1,149,551	3,610,349

The five leading States in pig iron production were as follows:

	Long tons.	Value.
Pennsylvania....	11,272,323	\$180,695,338
Ohio.....	5,752,112	88,122,356
Illinois.....	2,675,646	42,917,362
Alabama.....	1,939,147	23,754,551
New York.....	1,938,407	32,410,165

During 1910, of the 451 iron ore mines in operation, 191 mines produced over 50,000 long tons each, the largest quantity produced by a single mine being 3,190,093 tons, by the Hull-Rust mine, of the Mesabi range, Minnesota. Nine mines in Minnesota, besides one group of mines in Michigan and one group in Alabama, produced more than 1,000,000 tons each, the second greatest production being 1,769,067 long tons by the Red Mountain group of mines, near Birmingham, Alabama. Twenty-five mines produced more than 500,000 tons each.

Importations of iron ore in 1910 were the greatest in the history of the industry, being 2,591,031 tons, valued at \$7,832,225. Exports were 644,875 tons valued at \$2,074,164. Figures showing the foreign production of iron ore are not yet available for 1910, but the following table for 1909 shows the supremacy of the United States in iron mining.

United States.....	long tons..	51,155,437
Germany and Luxemburg.....	metric tons..	25,506,000
United Kingdom.....	long tons..	14,979,979
France.....	metric tons..	11,890,000
Cuba.....	long tons..	1,417,914

No other country produced so much as a million tons. It will be seen that the United States produced nearly one-half of the total of the world's output.

In steel production in 1910, Pennsylvania led all States, with 13,207,539 long tons and Ohio came second with 5,050,608 tons. The total production of the United States was 26,094,919 tons.

BAUXITE AND ALUMINUM PRODUCTION.

The United States Geological Survey reports that the 1910 output of bauxite in the United States was 148,932 long tons, valued at \$716,258. The average price at the mines has been: 1908, \$5.06; 1909, \$5.26; 1910, \$4.81. Bauxite is principally used in the production of metallic aluminum, and in the manufacture of the artificial abrasive, alundum, at Niagara Falls. This abrasive is made in the electric furnace by fusing calcined bauxite. Experiments are also being made in admixing bauxite with other materials for making refractory brick, which for linings far exceeds the life of silica or fire-clay bricks.

The world's production of bauxite in 1909 total 270,581 tons, valued at \$949,924, of which the American share was 129,101 tons, worth \$679,447. The French output was 128,099 tons, worth \$251,188.

The growth and magnitude of the aluminum industry in the United States are shown in the fact that only 83 pounds were produced in 1883, 3,000 pounds in 1886, 4,000,000 pounds in 1897, 17,211,000 pounds in 1907, 34,210,000 pounds in 1909 and 47,734,000 pounds in 1910. The American exports of aluminum and its manufactures increased from \$364,521 in 1906 to \$949,215 in 1910.

Under the Payne-Aldrich tariff act of August,

1909, aluminum scrap, and alloys of any kind in which aluminum is the component material of chief value, in crude form, are dutiable at 7 cents per pound, and plates, sheets, bars, and rods at 11 cents per pound instead of 8 cents and 13 cents, respectively.

The president of the Aluminum Company of America states that business in 1910 fell off on account of curtailed production in steel-making, in which it is used for deoxidizing and in the curtailed automobile business. "Large stocks accumulated and are still accumulating. Some plants have been cut back half and unless the demand improves still further cutting back will be necessary. The aluminum cooking utensil business was good. Although a new (aluminum) sheet-rolling mill was built in Niagara Falls in 1910, it was not put into operation, on account of the falling off in business, but as it was built to meet future requirements, it is expected that the time will come when the mill will be required."

The following is a summary of an article which appeared in the *Frankfurter Zeitung* of August 10:

"The development of the aluminum industry has been unusually rapid, the world's production having risen from 11,500 metric tons in 1905 to 24,200 metric tons in 1909, and 34,000 metric tons in 1910. The distinctive feature about the aluminum trade is that it is in the hands of only 12 companies, of which 5, viz., the Aluminum Industrie Akt. Ges., of Neuhausen, the Société Electro-Métallurgique Française, of Froges, the Compagnie des Produits Chimiques d'Alais et de la Camargue, of Salindres, the British Aluminum Company (Ltd.), and the Aluminum Company of America, account for nine-tenths of the total output."

WORLD'S CONSUMPTION OF BEER, WINE AND SPIRITS.

More beer is consumed in the United States than in any other country of the world, and more distilled spirits than in any other country except Russia. The quantity per capita consumed in the United States is not, however, in the case of beer, as great as in Belgium, United Kingdom, Germany, or Denmark, while our per capita consumption of distilled spirits is less than that of Denmark, Hungary, Austria, France, Netherlands, or Sweden. Of wines, the quantity consumed in the United States is below that of Portugal, Spain, Germany, Italy, or France; and the per capita consumption is less than that of France, Italy, Portugal, Spain, Switzerland, Austria, or Hungary.

The following table, compiled from official sources by the Bureau of Statistics, Department of Commerce and Labor, shows in millions of gallons the consumption of malt liquors, wines, and distilled spirits, respectively, in the principal countries of the world for which statistics of this character are published and the per capita consumption in each instance, the figures being for the latest year for which statistics are available.

Countries.		Consumption.					
		Malt liquors.		Wines.		Distilled spirits.	
		Million gallons.	per cap- ita.	Million gallons.	per cap- ita.	Million gallons.	per cap- ita.
United States	(1910)	1,851.3	20.09	60.5	0.66	133.5	1.45
United Kingdom	(1909)	1,397.3	31.44	15.2	0.31	40.1	0.96
Germany	(1909-10)	1,703.5	26.47	74.6	1.16	94.2	1.48
France	(1909)	375.0	9.51	1,541.4	39.36	70.9	1.81
Austria	(1908-9)	492.9	17.17	178.6	6.34	54.7	1.81
Belgium	(1909)	411.7	55.2	9.1	1.21	10.7	1.42
Russia	(1908)	231.4	1.46	no data	no data	232.7	1.45
Spain	(1909)	no data	no data	345.9	18.23	no data	no data
Sweden	(1908-9)	72.3	13.31	no data	no data	8.6	1.57
Switzerland	(1909)	64.6	18.00	52.2	14.55	3.6	0.99
Denmark	(1909)	61.7	22.98	no data	no data	8.0	2.97
Italy	(1909)	17.4	0.51	1,012.0	31.17	26.1	0.76
Bulgaria	(1909)	3.2	0.75	34.9	8.19	0.6	0.13
Hungary	(1908-9)	55.7	2.90	98.6	4.76	43.7	2.11
Netherlands	(1909)	no data	no data	2.3	0.40	10.8	1.84
Norway	(1909)	11.8	5.02	no data	no data	2.0	0.87
Portugal	(1909)	no data	no data	146.3	27.39	no data	no data
Roumania	(1909)	4.9	0.72	33.7	5.02	6.7	0.96
Servia	(1909)	2.9	1.02	10.5	3.70	no data	no data
Australia	(1909)	56.9	13.20	5.6	1.30	4.6	1.07
Canada	(1909-10)	47.4	6.36	0.9	0.12	7.3	0.97
Cape of Good Hope	(1909-10)	3.3	1.32	3.5	1.44	1.2	0.53
Transvaal	(1909)	3.9	2.88	0.5	0.38	0.8	0.67

REPORTS ON STREAM FLOW.

The United States Geological Survey has announced the publication of four reports on the flow of streams in the United States. They are designated as Water-Supply Papers 265, 266, 267 and 268. The first-mentioned relates to rivers in Minnesota, Wisconsin, North Dakota, Illinois, and Iowa, which drain either into the Mississippi River or northward into Canada. The second relates to rivers draining into the Missouri, the streams being located in Montana, Wyoming, North Dakota, Colorado, Nebraska, and Missouri. The third comprises those streams draining into the lower Mississippi mainly through Arkansas and Red Rivers, the streams being located in Colorado, New Mexico, Arkansas, Missouri and Mississippi. The fourth gives information concerning streams draining into the western part of the Gulf of Mexico, such as the Rio Grande and the Pecos.

The records contained in these reports show the flow of the rivers for each day during the year 1909 as measured by employees of the Geological Survey at permanent stations maintained along the streams. They are essentially a record of the performance of those streams and they furnish an account of the water resources available for use in the regions in which the records were made.

Many of those who are unfamiliar with engineering practice do not realize the necessity of procuring information of this kind. The importance of knowing how much water is available for its various uses grows enormously as the United States becomes more thickly settled and as industrial pursuits advance. We need water for domestic supplies and for navigation. The arid West is dependent on it for the irrigation of dry

lands. One of the most important features of our industrial prosperity has been the development of water power.

The four reports above described give a faithful record of each river's performance so that the persons or the community undertaking any development of water will know all the facts concerning the supply available.

INDUSTRIAL GAS APPLIANCE LABORATORY.

The Consolidated Gas Company, of New York City, has for several months been concerned in the work of fitting up an Industrial Gas Appliance Laboratory, in the Schleicher Building, corner of Second avenue and Twenty-second street.

The equipment of the laboratory contains, among other things, a six h. p. Otto gas engine, a three h. p. steam boiler, a combination tool-room furnace, clay annealer, melter, round annealer, bar annealer, forge, tool-room forge, oil tempering furnace, oven furnace, tempering furnace, rivet heater, muffle furnace with D. C. motor and fan blower, lead hardening furnace with extra pot for cyanide, muffle furnace with cupelling attachment, portable melting pot, 1,000 pound soft metal furnace with hood, wire basket and thermometer; brazing tables, automobile and wagon tire heaters, 40-gallon butchers' cauldron, 50-gallon cauldron with bottom draw-off, agitator and pump, china kiln, incinerator, oven with damper and thermometer, core-drying oven, japanning oven, aluminum water still, heating machines, positive blowers, confectioners' stoves—one with D. C. motor and blower—making in all 43 appliances standing on the floor. There are 75 bench appliances on metal tables, which, with a few suitably attached to the walls, make a total of 135 devices, all connected, ready for instant demonstration. The appliances on the tables embrace soldering furnaces and self-heating soldering irons, melting furnaces, glue heater, bench forges, rivet heaters, soft metal furnaces, and a great variety of burners, the largest being connected with D. C. motors and fan blowers, consuming about 700 cubic feet of gas per hour. A complete assortment of blowpipes and brazing burners is also in evidence. The appliances are located in sections, each section being served by a 30-light meter, with special reducing device which consists of a straight line control, the figures changing for each 10 feet, and so arranged that the counter can be turned back after each demonstration. Portable baths are also provided, one each for fresh or salt water; and for a cotton seed oil "dip," if one is so inclined. Then there is a portable sawdust drier, and the several things last enumerated are set on casters, so that one can readily be taken to any other appliance, the contiguity of which is needed for a complete demonstration.

PHOSPHATE MINING, 1910.

The mining of phosphate rock for fertilizer showed increased activity in 1910, with the greatest pro-

duction in the history of the industry. The output was 2,654,988 long tons, against 2,330,152 tons in 1909, an increase of 324,836 tons. Prices, however, were lower, the value of the 1910 output being \$10,917,000, or \$4.11 per ton, against \$10,772,120, or \$4.62 per ton, for 1909. Thus while the tonnage in 1910 increased 13.9 per cent., the value of the year's output increased less than 2 per cent. Nearly half of the phosphate rock produced in 1910 was exported, the shipments being 1,083,037 long tons. In 1909 the exports were 1,020,556 long tons. These and other statistics of production, exports, imports, etc., are given by F. B. Van Horn, of the United States Geological Survey, in an advance chapter from "Mineral Resources" for 1910.

According to Mr. Van Horn, there are at present five producing phosphate fields in the United States. In the order of quantity of production they are (1) Florida, (2) Tennessee, (3) South Carolina, (4) Arkansas, (5) Idaho, Wyoming, and Utah.

By far the largest of these fields is the Idaho-Wyoming-Utah field, where enormous deposits of high-grade phosphate rock, recently discovered, are available for mining. The field next in available unmined rock is probably Tennessee, where large areas are underlain by deposits of high-grade rock. Florida has a large reserve tonnage, but at the present rapid rate of mining it will not be many years before the rock will be exhausted.

MARKETED PRODUCTION OF PHOSPHATE ROCK IN THE UNITED STATES, 1901-1910, IN LONG TONS.

Year.	Quantity.	Value.
1901.....	1,483,723	\$5,316,403
1902.....	1,490,314	4,693,444
1903.....	1,581,576	5,319,294
1904.....	1,874,428	6,580,875
1905.....	1,947,190	6,763,403
1906.....	2,080,957	8,579,437
1907.....	2,265,343	10,653,558
1908.....	2,386,138	11,399,124
1909.....	2,330,152	10,772,120
1910.....	2,654,988	10,917,000

GYPSUM PRODUCTION.

The importance of the gypsum industry in the United States is shown by figures compiled by E. F. Burchard, of the United States Geological Survey. For 1910 the value of gypsum products was \$6,574,478 and the amount of gypsum mined 2,375,394 short tons. This was an increase over the figures for 1909 of more than 5 per cent. in tonnage and more than 10 per cent. in value. The value of the imports in 1910 amounted to only \$502,111, or less than 8 per cent. of the domestic output.

New York was the largest producer of gypsum, with an output valued at \$1,153,977, an increase of \$121,327 over 1909. Iowa came second with a value of \$943,849, and Michigan third with \$668,201.

The bulk of the gypsum produced was manufactured by grinding and partial or complete calcination into plaster of Paris, molding and casting plaster, stucco, cement plaster, fibered plaster, plaster boards, flooring

plaster and hard-finish plaster. The best known hard-finish, anhydrous plaster is Keene's cement, which sets very white and hard. It is used as a backing and surface for artificial marble and for ornamental moldings and castings, and its use as a wall plaster is increasing.

Refined grades of plaster are used in dental work, also as cement for plate glass during grinding, for making pottery molds, stereotype molds, and molds for rubber stamps, and as an ingredient in patent cements. A large quantity of gypsum is used in the raw state as a retarder in Portland cement. Considerable quantities are ground without burning and used as land plaster or in fertilizers. Smaller quantities are used unburned in the manufacture of crayons, paper, imitation meerschaum and ivory, calcimines, water paints and tints, and dry colors, notably Venetian reds. When used in excess in mixed paints, gypsum is regarded as an adulterant. The unburned and dead-burned forms of gypsum may be used to a certain extent with oil paints, because they are not very active chemically.

COAL PRODUCTION OF 1910.

For the first time in the history of the United States, the coal mines of the country in 1910 were credited with an output exceeding half a billion short tons, the combined production of anthracite, bituminous coal, and lignite having amounted to 501,576,895 short tons, with a spot value of \$629,529,745. This great output according to Edward W. Parker, Coal Statistician of the United States Geological Survey, was attained in spite of the fact that most of the mines in Illinois, Missouri, Kansas, Arkansas, and Oklahoma were closed for nearly six months by one of the most bitterly contested strikes in the history of the industry. The heaviest tonnage mined in any year previous to 1910 was in 1907, when a total of 480,363,424 short tons was produced.

The output in 1910 showed an increase of 40,762,279 short tons, or 8.85 per cent. Prices generally were a little higher in 1910 than in 1909, the average for Pennsylvania anthracite being \$2.13 per long ton, against \$2.06 in 1909, and the average for bituminous coal was \$1.12 per short ton in 1910, against \$1.07 in 1909. The total value increased 13.50 per cent.

The output of anthracite in Pennsylvania increased from 81,070,359 short tons, valued at \$149,181,587, to 84,485,236 short tons, valued at \$160,275,302, a gain of 4.21 per cent. in quantity and 7.44 per cent. in value. The bituminous production, including semi-anthracite, semibituminous, cannel, splint, and sub-bituminous coals, lignite, and a small quantity of anthracite from Colorado and New Mexico, increased from 379,744,257 short tons, valued at \$405,486,777, to 417,091,659 short tons, valued at \$469,254,443, a gain of 9.83 per cent. in quantity and of 15.73 per cent. in value.

The total increase of 40,762,279 short tons in 1910 over 1909 was equal to 20 per cent. more than the

entire output of the United States in 1870 and more than half of the total output in 1880.

INCREASING USE OF ELECTRIC FURNACES.

Prof. McWilliams, of the Sheffield University, in a report prepared for the meeting of the British Association at Portsmouth, gives some interesting figures relating to electric steel production. Up to June, 1910, there were about 118 electric furnaces of all types, of which 70 were in use, 10 were not working, and 38 were being built.

There were 77 arc furnaces recorded, of which 29 were credited to Héroult, 17 to Girod, 13 to Stassano, 6 to Keller, and 12 others. Of the induction furnaces there were 14 of the Kjelling type and 15 of the Rochling-Rodenhauser type. The total capacity of all electric furnaces was 350 tons per charge. In June, 1910, there were 29 Héroult furnaces with a capacity of 80 tons in use and furnaces of 50 tons in course of erection, while in June, 1911, there were 43 furnaces with a total capacity of 242 tons.

The output of electric steel in Germany, the United States, and Austria-Hungary in 1910 amounted to almost 112,000 tons, which is an increase of 63,000 tons over the figures of 1909. Those are the only countries for which the exact output of electric steel is published; probably the figures for Sweden, France, Belgium and Italy would also show large gains. The increase will likely be more than maintained in 1911, as more than 30 new furnaces of various types will be started during the year and many that started toward the end of 1910 will put in a full year's work in 1911. England will also, for the first time, appear as a regular producer, with an output of about 13,000 tons.

PRODUCTION OF PRECIOUS STONES, 1910.

It may perhaps be surprising to many people to learn that the United States produces almost every variety of precious stone—from diamonds down. The precious stones produced in this country last year had a value of \$295,797, against \$534,380 in 1909, according to an advance chapter from "Mineral Resources of the United States," on the production of gems and precious stones in 1910. The large decrease in the output of a few of the more important gem minerals—tourmaline, turquoise, chrysoprase, etc.,—readily accounted for the fall in the value of production. As an instance of this decrease in production, about 8 1/2 tons of rough turquoise were produced in 1910, as compared with more than 17 tons in 1909.

All the diamonds produced in this country in 1910 came from Arkansas and California, the output of Arkansas amounting to about 200 stones. Several diamonds were found in California last year, one of which weighs about half a carat and another between

1 3/4 and 2 carats. The latter is a brilliant, clear, flawless stone, with a tinge of yellow.

Colorado yields some very pretty agates and some are being successfully handled in the tourist trade but a number of these stones sold each year at the summer resorts of the State are imported from Germany, where they have been polished. Others are native stones polished abroad, although some are polished in the United States.

In Montana a sapphire weighing over 4 1/2 carats has been found. This stone when discovered had very much the shape of a rough diamond crystal, on account of which it had very great refractive power.

MINERAL WATER PRODUCTION.

In 1910 the sales of mineral water in the United States amounted to \$6,357,590, the product being 62,030,125 gallons, as reported by George C. Matson, of the United States Geological Survey. Minnesota was the greatest producer, with 9,962,370 gallons, derived from 19 springs. New York was a close second, selling 8,780,903 gallons from 46 springs. Wisconsin, however, obtained the greatest income from her mineral waters, her sales amounting to \$974,366; New York was second, with \$858,635; and Indiana third, with \$514,958. Minnesota's sales amounted to \$281,009. Louisiana has only four commercial springs: they produced 2,313,000 gallons.

Maine's output of mineral waters, from 29 springs, decreased 277,370 gallons, but on account of high prices increased in value over 1909, the figures for 1910 being 1,238,171 gallons and \$404,539. Of Wisconsin's mineral waters, 2,151,782 gallons were used in the manufacture of "soft drinks." Pennsylvania has 44 springs and produced 2,536,337 gallons, valued at \$221,685.

The mineral water trade continues to be prosperous although there was a decrease in output of about 4 per cent. as compared with 1909. The importation of mineral waters in 1910 was 3,306,303 gallons, valued at \$983,136.

FLUORSPAR.

Fluorspar, one of the lesser minerals, has come to occupy a comparatively important place in every-day affairs. It is used in the manufacture of glass, of enameled and sanitary ware, in refining antimony and lead, in the production of aluminum, and as a flux in blast furnaces and in the manufacture of steel in basic and open-hearth furnaces. The production of open-hearth steel alone in 1910 was over 15,000,000 long tons. The production of fluorspar, according to Ernest F. Burchard, of the United States Geological Survey, in a report on fluorspar and cryolite just issued, increased from 18,450 short tons in 1900, valued at \$94,500, to 69,427 tons in 1910, valued at \$430,196. There was an increase in 1910 of 37 per cent. in quantity and 47 per cent. in value over the

figures for 1900. The deposits which have been exploited are in Arizona, New Mexico, Colorado, Illinois, Kentucky, Tennessee, and New Hampshire. Illinois is much the heaviest producer. There was also imported in 1910, according to Mr. Burchard, 42,488 short tons, valued at \$135,152. Mr. Burchard's report contains, in addition to the statistics of the industry, a discussion of the methods of mining and milling fluorspar, as well as a description of recently discovered high-grade deposits in New Mexico.

THE DEVELOPMENT OF THE EXPORT OF AIR SALTPETER FROM NORWAY.

The export of this article shows yearly a large increase, although the total quantities are not yet very large. According to the review given out by the "Bureau Central de Statistique de Kristiania" the figures in 1000 tons of Norgesaltpeter in the years 1908-1910 are as follows:

Country to which exported.	1908.	1909.	1910.
Sweden.....	20.5	32	1.4
Denmark.....	538	256	392.2
Germany.....	3841	4803	4791
Holland.....	1270	1149	1687
Belgium.....	32	136	363
Great Britain.....	619	2530	4900
France.....	671	152	683
Spain.....	55.6	..	168
Italy.....	..	15	46
Ireland.....	..	250	200
Russia.....	..	21.5	100
Africa.....	5	12	..
U. S. of America.....	0.5	..	149
West Indies.....	..	2.2	10
Australia.....	..	7	39.6
Other countries...	0.1
Total.....	7052.6	9365.7	13530.3

The total export in 1910, therefore, amounted to 13,530 tons of saltpeter, of which Great Britain was the principal buyer, followed by Germany. All other countries use about one-half the amount exported to Great Britain and Germany. The price of Chile saltpeter has not yet been influenced by the importation of the air saltpeter.

CONCRETE AND CEMENT AT PANAMA.

The Isthmian Canal Commission have issued a statement showing that the total amount of concrete laid for the Panama Canal during the fiscal year 1910-11 was 1,742,928 cubic yards. The cost per cubic yard for concrete in the Gatun Locks was \$6.5919; in the Gatun Spillway, \$6.7044; in the Pedro Miguel Locks, \$4.7040; and in the Miraflores Locks, \$4.6826. At Gatun, 73,609 cubic yards of large rock were used, resulting in a saving of \$263,137.45, or of 0.2888 cent per cubic yard on each yard of material placed. In the production of stone for the concrete, the cost in bins at Gatun was \$2.3403 per

cubic yard, and in the storage pile for the locks on the Pacific side, \$0.8443 per cubic yard.

Cement for the large part is delivered in barrels to the Atlantic division at a cost of \$1.19 at tidewater in the United States, while in the Pacific division it is delivered in bags at a cost of \$1.60 at tidewater in the United States per barrel, less credit for return of bags. As approximately 90 per cent. of the bags were returned and accepted, the cement in bags cost \$1.01 per barrel at tidewater in the United States.

INVESTIGATION OF POTASH DEPOSITS.

An investigation into possible sources of potash salts in the United States is being made this year by the United States Geological Survey, and as a part of this work the Survey will soon fit up a temporary laboratory at Fallon, Nevada, for the purpose of testing samples of salines from the Great Basin or desert areas.

Samples of such alkaline salts will be tested at this laboratory free of charge if a definite statement of the locality from which they were obtained be sent with the samples. The location should be given by section, township, and range, if possible, otherwise by distance and direction from the nearest post-office or settlement. Samples should be addressed to Hoyt S. Gale, United States Geological Survey, Fallon, Nev. Upon receipt of a request small sample sacks for sending the material by mail will be forwarded from the above address.

If so requested at the time that a sample is submitted for test, the accompanying information concerning the locality of the deposit will be treated as confidential; and the evidence thus obtained is not to be used for the purpose of making land withdrawals.

CORROSION OF SUPERHEATED STEAM PIPING BY SODA.

Mr. F. Westhoff recently reported (*Stahl und Eisen*, June 29, 1911) to the Dusseldorf convention of the Deutsche Giessereitachleute that in a boiler plant working partly with saturated and partly with superheated steam (at 160 lbs. gage), the wrought-iron pipes and cast-iron valves of the superheated steam line were badly attacked after four years' service, whereas the saturated steam line was in excellent condition. Appearances suggested local solvent action. On close examination a whitish matter was found at the corroded places, which, on chemical analysis, proved to be in part at least sodium carbonate. Soda was used for softening the feed, and it seemed that the amount used was rather excessive; 1 1/3 days after blowing down the boilers the boiler water showed 21.2 grams soda per 100 liters, or 12.4 grains per gallon. The investigator concluded that soda particles were carried along with the steam, and that in the superheated steam line they could deposit, while with saturated steam the condensation flow prevented

deposits. He concludes that this deposited soda corroded the iron.

A STANDARD PORTLAND CEMENT SPECIFICATION.

United States Government work is being looked into by a special committee of government engineers, which has been meeting during the past summer. This committee was appointed to draw up a tentative specification by a conference of government engineers that first met in Washington, D. C., on June 17, 1911. The draft of this specification was submitted later to the conference and proved acceptable in most particulars. The committee was then instructed to consult with the American Society of Civil Engineers the American Society for Testing Materials and other similar bodies as to the practicability of developing a uniform specification that might become a generally accepted standard throughout the United States.

The committee is composed of A. P. Davis, Chief Engineer, U. S. Reclamation Service; J. C. Plant, Supervising Architect's office; Captain W. R. Rose, Corps of Engineers, U. S. A.; Lieut. C. A. Carlson, Corps of Civil Engineers, U. S. N.; S. S. Voorhees, Bureau of Standards; A. E. Phillips, Superintendent of Sewers, District of Columbia; and R. J. Wig, Bureau of Standards.

MINERAL PRODUCTION SECOND ONLY TO AGRICULTURE.

Nearly a third of a billion dollars was added to the wealth of the United States from the mineral production of the western States during 1910, according to the figures of the United States Geological Survey. This includes about \$66,000,000 worth of coal, the remaining production, principally metals, having a value of practically a quarter of a billion dollars. The total figures of western mineral production as compiled by the Survey are \$313,944,881. This is about one-fourth the total agricultural production of the same area, the proportion between mineral and agricultural production being about the same as for the entire United States. The agricultural production of the western States, derived from figures of the Department of Agriculture, was approximately \$1,394,791,000. The area considered includes the belt from the Dakotas south to Texas and the territory westward.

PRODUCTION OF LIME IN 1910.

The total production of lime in 1910, according to figures compiled by Ernest F. Burchard and just given out by the United States Geological Survey, was 3,469,416 short tons, valued at \$13,809,290, a slight decrease in both tonnage and value as compared with the figures for 1909. The average price per ton in 1910 was \$3.98.

The five leading States in the 1910 production are as follows:

	Short tons.	Value.
Pennsylvania.....	877,714	\$2,440,350
Ohio.....	415,285	1,647,335
Wisconsin.....	248,238	959,405
Maine.....	179,656	893,599
Missouri.....	193,964	837,681

OIL USED IN PLACE OF COAL.

The small production of coal in California is offset by the enormous increase in the production of petroleum, most of which is used for fuel. The oil produced in California in 1910 aggregated between 65,000,000 and 70,000,000 barrels, which, on the basis of $3\frac{1}{2}$ barrels of oil for each ton of high-grade coal, would be equal to a production of nearly 20,000,000 tons of coal.

The use of petroleum by the transportation and manufacturing industries of California has practically eliminated coal as a steam-raising fuel in the State. Oil is also used in the manufacture of gas which is employed for cooking and for heating residences as well as for lighting. Oil is now also coming into use as a direct fuel for household purposes.

NEW JERSEY'S ZINC PRODUCTION.

The zinc mines, at Franklin Furnace, New Jersey, produced in 1910, according to H. D. McCaskey, of the United States Geological Survey, 308,353 tons of ore for the concentrating mills (producing 263,606 tons of concentrates), and 67,324 tons of crude ore for the smelters. Figured as metallic zinc, the total recoverable output was 137,355,219 pounds of spelter, valued at \$7,417,182. The mines are opened by a vertical shaft 965 feet deep, a slope to the 600-foot level, and a shaft 1,500 feet deep on an incline of $47\frac{1}{2}$ degrees. The crushing plant has a capacity of 2,240 net tons per 24 hours and the separator a capacity of 1,344 net tons.

WORLD'S SULPHUR PRODUCTION.

The sulphur industry in the United States in 1910 was confined to the four states of Louisiana, Nevada, Utah and Wyoming, the production of the other states being practically negligible as compared with that of Louisiana. The production of sulphur for 1910, according to W. C. Phalen, of the U. S. Geological Survey, was 255,534 long tons, as compared with 239,312 long tons in 1909. In 1910 there were imported into the United States 30,833 long tons of sulphur, while the exports amounted to 30,742 long tons.

SICILY SULPHUR PRODUCTION.

The total production of sulphur in Sicily during the first six months of 1911 was 182,678 tons, against 185,825 tons during the corresponding period in 1910.

On June 30, 1911, the total stocks of sulphur in Sicily were 527,965 tons, against 586,878 tons at the same date in 1910. The exports of sulphur during the first half-year of 1911 amounted to 287,410 tons, against 240,919 during the first six months of 1910, an increase of 46,491 tons.

SALT PRODUCTION, 1910.

The United States produced 30,305,656 barrels of salt in 1910, valued at \$7,900,344, according to the U. S. Geological Survey. This was an increase of 198,010 barrels over the production of 1909 but a decrease in value amounting to \$443,487. The six leading producers of salt in 1910 were New York, Michigan, Ohio, Kansas, Louisiana, and California. Nearly 99 per cent. of the salt consumed in the country was obtained from domestic sources, the United States having long been independent of foreign production.

PLATINUM PRODUCTION, 1910.

The entire production of crude platinum from placer mines in the United States for last year, as well as for 1909, came from the States of California and Oregon. This production in 1910, according to Waldemar Lindgren, of the United States Geological Survey, was 390 troy ounces, valued at \$9,507, a decrease of 282 ounces and \$3,296 compared with the figures for 1909.

INTERNATIONAL MACHINERY AND ENGINEERING EXHIBITION.

An International Machinery and Engineering Exhibition will be held at Olympia, London, from October 4 to 26, 1912, inclusive. This Exhibition is organized by the Machine, Tool and Engineering Association (Ltd.), and the Exhibition offices are at 104 High Holborn, London, W. C.

The projectors of the Exhibition state that it is their purpose to secure, if possible, so comprehensive a display that it will be really representative of the engineering trades throughout the world.

MODIFICATION OF THE DETERMINATION OF NICKEL BY THE ETHER METHOD.

Owing to the length of time necessary for the determination of nickel in iron and steel by the usual ether method which involves solution in nitric acid and several evaporations to dryness and baking prior to the ether separation, I have been working toward a shorter method. This has been found by using hydrogen peroxide as an oxidizing agent in place of nitric acid. By this change in method, determinations can be made in one-fourth the time and with just as consistent accuracy.

Method.—Dissolve one gram of the sample in a mixture of 20 cc. of hydrochloric acid and 5 cc. of water using a 200 cc. beaker. Cover with a watch glass and heat until solution is effected. When the sample is dissolved cool the solution a little, add 20 cc. hydrogen peroxide (washing the sides of the beaker and watch glass) and boil to a small bulk, about 10 to 15 cc. Cool and make ether separation in the usual way.

The nickel is determined volumetrically in the usual way making the solution ammoniacal and titrating with potassium cyanide using silver nitrate and potassium iodide as an indicator.

CARPENTER STEEL COMPANY,

READING, PA.,

October 12, 1911.

JOHN P. THOMPSON.

GENERAL NOTES.

Dr. Cushman announces the organization and equipment of a Division of Roads and Pavements under the supervision of Mr. Prévost Hubbard, for the past seven years with the U. S. Department of Agriculture, as chief chemist of the Office of Public Roads.

The Division of Roads and Pavements has been assigned adequate quarters in the Institute's new building, which has just been completed, and will consist of two well equipped laboratories—one for physical work in connection with cements, mortars, concrete block, brick, etc., and the other for chemical analysis and investigations of all types of bituminous and other road and paving materials. The equipment consists of the latest approved apparatus, and special apparatus will be added as occasion demands.

Besides the routine examination, inspection, and specification of road and paving materials which will be undertaken by this Division, the Institute particularly solicits correspondence relative to problems connected with the road material industries, in regard to improvements of materials and processes, and the utilization of waste and by-products.

Ground was broken last week for the Wolcott Gibbs Memorial Laboratory of Harvard University. This building, designed for research in physical and inorganic chemistry, will cost when completed about \$72,000. It was given and endowed by Dr. Morris Loeb, Mr. James Loeb and many other friends of Dr. Gibbs and the University.

Mr. Arthur H. Blanchard, M. Am. Soc. C. E., consulting highway engineer, formerly of Providence, R. I., announces the removal of his office and laboratory to Broadway and 117th Street, New York City.

Sugar beets in Canada from the 12,000 acres this

season are expected to yield 9,000 long tons of sugar, against 7,771 tons from 10,500 acres last year. Canada imported 574,108,164 pounds of sugar, valued at \$15,110,740, in the fiscal year ended March 31, 1911.

American imports and exports both made large gains in September, being \$125,160,444 and \$193,623,232, in value, respectively, advances of \$7,895,931 and \$27,677,012 over September, 1910.

CONSULAR AND TRADE NOTES.

INTERNATIONAL RUBBER EXHIBITION.

By Consul General John L. Griffiths.

The most interesting feature of the International Rubber Exhibition held in London, June 24 to July 14, was the evidence of the great growth of the rubber industry in the past few years, and the multiplied uses for which rubber is now employed.

The greatest demand for rubber is, of course, in the boot and shoe industry, and in the manufacture of motor and cycle tires. The variety of purposes for which rubber in some form is employed was shown at the exhibition in displays of golf and tennis balls, mackintoshes, fountain pens, air pillows, water beds, cables, buckets, mats, and tiling, etc.

The principal subjects discussed at the conference were rubber cultivation, the preparation of rubber, and rubber manufactures.

The planter, manufacturer, machinist, and chemist were brought into touch with each other and an opportunity afforded for the interchange of views.

The principal countries exhibiting were Brazil, Ceylon, Federated Malay States, Belgium, Holland, Germany, South India, Uganda and the West Indies.

The special medal for the best exhibition of rubber was awarded to the State of Amazonas, Brazil. This exhibition consisted of 20 tons of rubber and 5 tons of cauchó ball, representing approximately the one-thousandth part of the rubber passing annually from Manaus. In 1901-2, 19,989 tons of rubber and cauchó were received in Manaus from the State, inclusive of that in transit from Peru, Bolivia, and Venezuela. In 1909-10 this total had risen to 30,065 tons. This was natural or "wild" rubber, from vines and trees indigenous to the soil.

The Federated Malay States and Straits Settlements figure largely as present and prospective rubber producers. The quantity harvested practically doubles each year; in 1906 there were 1,035,601 pounds exported; in 1907, 1,989,889 pounds; in 1908, 3,186,099 pounds; in 1909, 6,112,023 pounds; and in 1910, 12,245,864 pounds. In view of the large acreages put under rubber during recent years, it is anticipated that equal increases will be shown in the future.

In 1842 and for many years all rubber was derived from wild plants, and the method of collecting it destroyed vast numbers of trees and vines, until it seemed probable that the supply of rubber would soon be exhausted. In 1876 Mr. Wickham was commissioned by the authorities at Kew Gardens to proceed to the Amazon Valley to secure a supply of Para rubber seeds. He brought back about 70,000 seeds, from which nearly 2,800 plants were raised at Kew Gardens and exported in miniature hot-houses to the Botanic Gardens at Ceylon. From these plants additional seeds were obtained. At the same time plants were introduced into Singapore, and seeds were sent from there to Borneo, Perak and elsewhere.

In 1884 tapping cultivated trees first took place in Ceylon, and in 1888 in Singapore, but not until 1899 was the first sheet rubber (from trees in Perak) sold in London—the first cultivated Para rubber placed upon the European markets. In considering these facts, one must be impressed with the rapid growth that has since taken place.

In Ceylon, for example, notwithstanding that thousands of acres are given over to tea, rubber cultivation is one of the most important planting industries. Although the island

does not possess any indigenous rubber-yielding plants, the climate and soil have proved very suitable for the growth of Para, Ceara, and Castilloa rubber trees—the first named in particular. In 1900 it is stated that only 1,750 acres were under rubber in the whole island; but since then the development has been extremely rapid. In 1910 it was estimated that no less than 200,000 acres were planted with rubber.

The average cost of establishing a rubber plantation in Ceylon, and maintaining it up to the sixth year, is estimated at £25 (\$121.66) per acre, apart from the cost of the land. Tapping can usually be commenced on trees 5 years old, and about 150 pounds per acre are obtainable in the seventh year, after which there is a considerable increase. Plantation rubber from Ceylon has, it is claimed, usually realized prices slightly in excess of those of fine Para from South America. The Ceara tree (at first unsatisfactory) can now be grown in situations in the island which are unsuitable for Para trees. When well prepared, Ceara rubber obtains prices equal to plantation rubber.

The growth of the rubber output of Ceylon is shown in the following statement: In 1903, 18½ tons; 1904, 34½ tons; 1905, 75 tons; 1906, 146 tons; 1907, 248 tons; 1908, 407 tons; 1909, 666 tons; 1910, 1,601 tons. The output for 1911 is estimated at 2,230 tons. It is thought a total crop of 30,000 tons will be realized in 1920.

British Guiana is being opened up and placed under the cultivation of rubber and balata. Of the latter over 1,000,000 pounds are annually exported, the demand for it continually increasing, especially in the United States. Licenses for its collection are issued for terms not exceeding 15 years, and the major portion of the easily accessible lands have been leased. As regards rubber, there are 9,000,000 acres of lands of easy access still unalienated and 36,000,000 of hilly lands; of this 45,000,000 of acres, a very large portion is stated to be suitable for rubber cultivation, the costs of which are low, it being possible to plant land at a cost of \$68 per acre for the first year, with an annual expenditure of about \$29 per acre in subsequent years.

Trinidad and Tobago are among the latest producers of rubber. The kinds most extensively grown are Hevea (Para) and Castilloa, while some Ceara and Funtumia are produced in the drier localities. It is stated that there are many thousands of acres in the southeastern part of the island suitable for rubber cultivation (of the two first-named varieties) which are not yet alienated, and which can be purchased by settlers at \$12.25 per acre, survey included. The growth of the industry in Tobago is shown in the increase of the exports of rubber from 91 pounds in 1904 to 4,348 pounds in 1910, notwithstanding the fact that the trees are young and that only a small area has been tapped.

In recent years Dominica has been extensively planted with rubber—Hevea and Castilloa—and it is stated the growth is luxuriant, and results demonstrate that the islands are well suited for rubber cultivation. The Crown lands comprise about 100,000 acres, and are sold at \$2.45 per acre. The payment for blocks exceeding 100 acres can, if desired, be spread over three or four years.

German as well as British East Africa is fast becoming a factor in the world's supply, together with Uganda, while in

Mexico tapping has been going for years. On one plantation (La Zacualpa) there are nearly 4,000,000 trees (of the Castilloa variety). This and a sister plantation showed live trees at the exhibition, from which demonstrations were given of tapping (or "milking") and collecting the latex which, by the use of centrifugal machines, can be converted into solid cones within half an hour. By this process, it is claimed that sheet rubber to suit the market is ready for shipment in three hours, as compared with three days by the ordinary method.

Although the total quantity of rubber exported from Uganda since 1902 has amounted to only 467,040 pounds, valued at \$250,000, this was derived chiefly from vines. Ceara was introduced in 1902, and has been found a valuable addition to the country's resources. Three-year-old trees yield an average of 30 ounces of dry rubber per annum, while 8-year-old trees yield 19 ounces in 2½ months. Tapping is on the "half herring-bone" system, every alternate day, to a height of 4 feet. Para was introduced in 1901, and makes excellent growth; an 8-year-old tree attains a growth of 35 inches, and yielded 16½ ounces of dry rubber in 107 tappings.

Castilloa and Manicoba plants are not recommended for Uganda, the former being subject to attack by a boring beetle and the latter slower in growth than Ceara. There are, it is stated, several rubber plantations in the country, and plants are making rapid and strong growth. The cost of land (freehold) is about 65 cents per acre.

In view of the growing output, which is due not only to the increasing acreage, but also to the fact that as trees develop they give a larger yield each year, it is held by some authorities that the time is approaching when the supply will exceed the demand. Shrewd judges, however, are not of this opinion, because new uses for rubber are constantly being found, and in their view there is a field for much further utilization. White rubber is now extensively used in surgical, medical, and scientific apparatus and appliances, household requisites, and to an enormous extent, for tires. In addition to many other ways, it has yet to be used as a paving in cities in a general direction. Although this use is not new, the chief drawbacks at present are its cost and the need of a perfected method of manufacture.

Samples of rubber paving were laid down in the exhibition by a British company; and recently banks and insurance companies and other large buildings have utilized it in this way. In the opinion of the president of the exhibition, "the problem had made great strides," and he "felt sure before long a process for the application of rubber to street paving would be perfected."

The exhibit of one of the American companies which attracted a good deal of attention was a miniature rubber factory demonstrating modern methods of using guayule rubber in various rubber goods on the market. The process of extraction of rubber from the shrub (a native of Mexico) was indicated by samples taken at different points of manipulation. First, it was shown how the rubber is washed and sheeted; then dried by a high vacuum and low-temperature method. The rubber is next put on the mixing mill, and can be easily worked to requirements. Guayule, it is claimed, is better than it looks. In appearance it is a "somewhat low, softish rubber," but vulcanizes remarkably. Blended with other rubber, it is practically suitable for any grade of goods, and is being used on a large scale. The estimated amount produced in 1910 was 28,500,000 pounds, of which this company produced 15,000,000 pounds. It is marked in a clean condition in bags weighing about 150 pounds. According to the company's statement, guayule is successfully employed in making all classes of belting, packing, hose, valves, mats, disks, and a thousand and one molded articles for all purposes, as well as entering into the composition of boots, shoes and tires.

An American rubber mill machinery manufacturing firm

exhibited various machines in connection with the guayule miniature factory exhibit. The machines were not of full size, but were very complete.

In addition to the numberless kinds, classes, and grades of rubber shown, there were exhibits of coconuts, sisal hemp, oilseeds, catchcrop beans of various kinds (including soya beans from the British East African Protectorate), and kapok. The latter was exported from German East Africa and appeared to be of excellent quality. It is not, however, on the London market, but is shipped to Hamburg for sale and export.

In an interesting article written by Mr. Walter Freudenberg, of Bremen, the future supply of rubber is dealt with. He quotes the estimated planted acreages as given by three of the leading trade publications: India Rubber Trades Diary, 776,000 acres; India Rubber Journal, 980,000 acres; Gummi-Zeitung (Berlin), 1,310,000 acres; and he takes the second as a basis for future yields: From Malaya (authority, Sir John Anderson), 70,000 tons; Ceylon (authority, Ceylon Observer), 19,000 tons; Dutch Indies, Borneo, South Mora and Burma, 20,000 tons; total annual supply of plantation rubber in 1916-17, 109,000 tons. To this must be added the probable supply of wild rubber, which until recently has been about 70,000 tons annually. He considers, however, that the supply from this source may decrease, in view of the larger crop of plantation rubber, and estimates only 35,000 tons, making a gross total of 144,000 tons in 1916-17.

As to the present and probable future consumption, it would appear from available statistics that for the year ending June 30, 1910, a total of 76,000 tons was used, showing an increase of about 5 per cent. annually during the past 10 years; and if this rate of increase continues, about 107,000 tons would be required by 1916-17. But this rate of increase does not, of course, take into consideration new uses to which rubber may be put.

The imports of raw rubber by the United Kingdom, Germany, Belgium and the United States, the five principal users, for the first five months of 1911, and for the years 1909 and 1910, are shown in the following table (in long tons):

	First five months.	Twelve months.	
	1911. Tons.	1910. Tons.	1909. Tons.
United Kingdom.....	20,000	44,000	35,000
Germany.....	8,400	18,700	15,550
Belgium.....	4,570	10,550	8,550
France.....	9,020	19,980	15,220
United States ¹	28,773	87,352	60,312

NOTE.—This table should not be understood to represent the actual quantity of rubber produced in the years indicated, the figures including transshipments from one country to another.

UTILIZATION OF WASTE METALS.

Figures showing the recovery of "secondary" copper, lead, zinc, tin and antimony in the United States in 1910 are summarized by the Geological Survey in the table below. The secondary metals include those recovered from scrap metal, sweepings, drosses, etc. They are called "secondary" to distinguish them from the metals derived from ore, which are known as "primary" metals.

The table gives the quantity and value of each secondary metal recovered during the years 1909 and 1910. The large increase shown in the figures for 1910 was occasioned partly by increased business activity and the growing tendency toward conservation, but is explained in part by the fact that in 1910

¹ Including balata, guayule, gutta-percha, gutta-jelutong, and scrap rubber.

the Survey made a more extensive canvass of the sources of production. As these secondary metals displace equal quantities of primary metal in supplying consumption, they undoubtedly affect the prices of primary metals to some extent now and will affect them even more in the future.

Metals.	1909.		1910	
	Short tons.	Value.	Short tons.	Value.
Secondary copper, including that in alloys other than brass.....	25,396	\$6,602,960	51,000	\$12,954,000
Remelted brass.....	27,347	5,863,181	62,000	13,032,400
Secondary lead.....	17,822		29,384	
Recovered lead in alloys.....	23,327	3,538,814	25,939	4,868,400
Secondary spelter.....	33,040		41,223	
Recovered zinc in alloys other than brass.....	1,181	3,695,868	2,709	4,744,300
Secondary tin.....	2,423		7,217	
Recovered tin in alloys.....	3,092	3,281,425	6,686	9,481,800
Secondary antimony.....	27		9	
Recovered antimony in alloys.....	1,529	257,362	2,770	444,600
Total value.....	..	23,239,610	..	45,525,500

The total amount of secondary copper recovered, on the assumption that the brass remelted had an average copper content of 70 per cent., was 91,500 tons, of which 15,500 tons was recovered by regular refining plants and the remainder by plants treating only secondary material. At least 30,000 tons was recovered from clean scrap made in the course of manufacture of copper and brass ware, so that only 61,500 tons were obtained from ashes and cinders and from material that had entered the trade in manufactured form and been discarded. The Survey inquiry was extended so as to include the railway companies' figures for old metals reused by themselves, and to these is attributed a large proportion of the increase in the figures for copper. The production from secondary sources in 1910 was equal to about 17 per cent. of the domestic consumption of new copper.

The secondary lead was equal to 11.5 per cent. of the refined lead produced in the United States.

The secondary zinc (including that in brass) equals 23.2 per cent. of the total production as primary spelter in the United States.

The secondary antimony (recovered almost wholly in alloys) shows a large increase and, as the production from domestic antimonial lead ores was comparatively small, the secondary recoveries are the only important domestic source of supply.

The production of tin from ore mined in the United States is negligible, so that the secondary recoveries constitute practically the sole domestic supply. The figures for 1910 recoveries show a large increase over those for 1909, mainly because the quantity of metal recovered from scruff and drosses from tin andterne plate manufacturers was ascertained. There were also several plants which made tin oxide and tin chloride from clean scrap tin. The production of these compounds is calculated as metal to avoid disclosing the output of products having a limited use. Although a large quantity of tin is recovered from scrap by electrolytic treatment, and a smaller quantity is converted directly into oxide and chloride, the principal recovery is made from scruff and drosses, or in alloys.

hop crop are now available, and while the crops in Bavaria and Bohemia, where the finest hops are grown, are only about half those of 1910, the figures show that the world's crop this year was only about 230,000 hundredweight less than that of last year. The area planted to hops in Bavaria was slightly less than last year, while in Bohemia it was practically the same, and in the world as a whole it was only a few hundred acres larger. Brewers who must have the prime Bavarian and Bohemian hops must this year pay high prices, shipments now (Sept. 29) being invoiced at from 70 to 80 cents per pound from Nuremberg; but on the whole there are no indications of a shortage in hop supply.

ACREAGE AND CROP OF THE WORLD

The following tables give the area planted and total crop of the world for the last three years, the hundredweight used meaning bales of 50 kilos, or 110 pounds.

Countries.	Area planted.			Total crop.		
	1909. Acres	1910. Acres	1911. Acres	1909. Cwt.	1910. Cwt.	1911. Cwt.
Germany.....	71,568	67,867	65,934	119,000	384,000	222,000
Austria-Hungary	58,148	52,194	51,826	164,000	297,000	178,000
France.....	6,920	6,920	6,920	27,000	54,000	45,000
Belgium and Netherlands...	5,204	4,793	4,942	29,000	58,000	52,000
Russia.....	20,786	22,407	22,240	60,000	58,000	62,000
England.....	32,565	32,911	34,595	205,000	296,000	354,000
America.....	43,635	44,478	46,950	310,000	400,000	400,000
Australia.....	1,853	1,828	1,828	10,000	10,000	15,000
Total	240,679	233,398	235,235	924,000	1,557,000	1,328,000

The figures for Germany and Austria-Hungary in the foregoing table are based upon complete and semiofficial reports from all hop-growing districts, and those for other countries upon very full reports received by one of the oldest and most reliable firms of hop dealers in this market, and they may be accepted as the best figures at this time obtainable.

RUSSIAN CROP ESTIMATES.

Consul John H. Grout submits a Russian trade journal estimate of the probable amount of grain to be expected in Russia this year. This estimate is based upon statistics gathered between the first and the middle of July last, and is given in the following table, together with the totals for 1910, and the average crop from 1906 to 1910:

Class of grain.	Average crop.		
	1906-1910. Tons.	1910. Tons.	1911. Tons.
Winter rye.....	21,280,600	23,839,200	22,154,400
Winter wheat.....	5,839,200	7,437,600	5,839,200
Spring rye.....	496,800	376,200	291,600
Spring wheat.....	12,218,400	15,757,200	12,979,800
Barley.....	8,922,600	11,064,600	10,443,600
Buckwheat.....	1,126,800	1,346,400	984,600
Millet.....	2,417,400	2,899,800	2,039,400
Maize.....	1,431,000	2,165,400	1,704,600
Oats.....	14,833,800	16,654,200	14,680,800

Since the foregoing estimate was made, there has been considerable deterioration of the crops. It is possible that a reduction of something like 5 per cent. to 10 per cent. may safely be made in order to arrive at a reasonable estimate of the results of the 1911 crop. Aside from the matter of quantity, reports are arriving to the effect that quality has suffered as well, at least in many parts of the country.

THE WORLD HOP CROP.

Consul George Nicolas Ifit reports that statistics of the 1911

PIG IRON PRODUCTION OF JAPAN.

Consul General Thomas Sammons reports that an estimate

supplied by the Department of Finance places the production of iron in Japan for 1910 at 71,963 tons, valued at \$1,410,685. The average production for the past 10 years has been 50,030 tons, valued at \$1,010,529, but the output has been increasing, the figures for 1901 having been 32,455 tons, valued at \$602,196.

During 1910 Japan imported pig iron to the extent of 117,227 tons, valued at \$1,675,371, of which 98 per cent. came from Great Britain, and less than one-tenth of 1 per cent. from the United States. The remainder was divided between China, Sweden and Germany, in that order.

Japan also imports iron ores, 208,191 tons having been received in 1910, with a value of \$579,819, of which China supplied 61 per cent., Korea 35 per cent., and Great Britain 3 per cent., the 1 per cent. remaining coming from other countries.

CANADA'S TIMBER RESOURCES.

An official publication of the Dominion forestry branch of the Department of the Interior says: "The original timber area, omitting semitreeless lands, was approximately 1,900,000 square miles; 98,000 square miles have been cleared for settlement, and 100,000 square miles have been cut over by lumbermen, leaving a timbered area yet untouched of 1,702,000 square miles. Assuming the average of 3,000 feet per acre, there should yet

remain 3,370,000,000,000 feet of timber in Canada at a very conservative estimate. The highest estimate that has been made hitherto, that given by the conservation commission, places the amount of saw timber and pulp wood in Canada at 494,600,000,000 feet and 1,100,000,000 cords, respectively." The forest area of Canada has been variously estimated by experts from time to time, but the above figures seem to be the most accurate the Government ever issued on the subject.

CLAY-PRODUCTS EXPOSITION.

An exposition covering the clay-products industries will be held in Chicago, March 7 to 12, 1912, and the early plans promise the most complete display of the various lines comprised in this industry that ever has been provided.

At the time of the exposition there will be a number of conventions of organizations which are allied with the clay-products industries. Among those which, according to the Construction News, will meet at this time are the National Brick Manufacturers' Association, the National Paving Brick Manufacturers' Association, the Building Brick Association of America, the Clay Machinery Manufacturers' Association, the American Ceramic Society, the Illinois Clay Workers' Association, and the Middle West Clay Workers' Association.

BOOK REVIEWS.

Modern Industrial Chemistry. By H. BLÜCHER. Translated from German by J. P. MILLINGTON. 779 pages. 15 full page illustrations; 25 pages advertisements. Gresham Publishing Co., London. D. Van Nostrand Co., New York. Price, \$7.50 net.

This book is obviously not intended for use as a text-book, but is essentially, on account of the arrangement of material and range of subjects, a small reference encyclopedia.

Subjects are arranged in alphabetical order and the author has exercised a startling liberty in selecting material for discussion under the general title of *Modern Industrial Chemistry*. In this connection one is somewhat surprised to find space given to such subjects as Accidents, including directions for "Treatment of Frozen People," "Sunstroke," "Poisoning," etc. Granting that these are important directions to have within the reach of factory chemists, it is not likely they would think of looking in a volume on *Industrial Chemistry* for such emergency information. Artificial Diamonds (page 219) has been given almost a page, with no qualifications as to the commercial importance of this as an industry. The lack of a sense of proportion so common in works on *Industrial Chemistry* is one of the most conspicuous features of this book. Industries of little or no productive or typical value are discussed at length, while some of our greatest industrial propositions are dismissed with a paragraph or two. At least half of the material is general descriptive data, to be found in text-books on chemistry or physics.

Ambiguity is a conspicuous feature in many of the statements. It is doubtful if a clear conception of a filter-press would be established in any one's mind by reading this description (page 274): "A

filter-press consists of a series of boxes between two strong head-pieces, one movable and one fixed (the latter on stand), resting on two strong side spindles and lined with some suitable filtering material." Again, the statement is made, under Cellulose (page 150): "Among the fiber substitutes used in the manufacture of paper, mechanical wood pulp and cellulose should be mentioned. For the former Cf-WOOD. Cellulose differs from wood pulp in that it is a pure chemical product free from impurities."

The subject of Cement is disposed of in less than two pages. The statements are so involved, and so far from representing the modern industrial practice, that it would be a calamity to have this fall into the hands of a student or one seeking general information on this important industry.

Under the heading of "Gaseous Fuels" (page 287), the author enumerates coal gas, oil gas, wood gas, producer gas, and acetylene. The reviewer is not familiar with the use of acetylene for fuel purposes, but recalls that millions of cubic feet of natural gas (not mentioned) are used annually.

Patents are frequently referred to by numbers and country, and the quantity of such references creates a doubt as to their real importance in the advancement of the industry under consideration. Frequent reference is also made in the notes, to advertisers who have taken space in the 25 pages of the book devoted to that purpose.

The reviewer is at a loss to determine just what is the purpose of such a book. The collection of an indiscriminate lot of general physical and chemical data, much of which is simple definition, compiled without regard to the commercial importance of the

subject under discussion, with very few attempts to describe or illustrate the logical steps of manufacture, and arranged in alphabetical "taggedness," is obviously unlikely to produce a book on Modern Industrial Chemistry. Such a book would have a doubtful value, either to the lay reader, the student, or works manager. A promise by the author or the translator might have suggested their error at this point, but we were denied this helpful suggestion, and instead favored with a monograph on the value of the work by the publisher.

M. C. WHITMAN.

Lubricating Oils, Fats and Greases. By GEORGE H. HURST. Third Edition. Revised and enlarged by HEAVY LOST. 366 pp. Scott, Greenwood & Son, London. D. Van Nostrand Company, New York, 1931. Price \$3.00.

This third edition of Hurst's well-known book, while enlarged and improved, retains in the main the characteristics of the two former editions. It deals with the subject as is natural, largely from the standpoint of the English user of oils; the description in Chapter III of the Scotch Shale Oil Industry is full, and is brought up to a recent date while Chapter IV on Petroleum, though sufficiently complete for the probable user of the work, takes little account of the more recently developed fields of petroleum and the products peculiar to them.

The chapter devoted to Vegetable and Mineral Oils and Fats gives a good general view of the subject although in many details, particularly in the statements of the "Constants of Oil," erroneous ideas would be derived by the casual reader, as for example, the statement of the specific gravity of each oil in the fourth place of decimals as though it were a fixed and unchanging characteristic of the particular oil in question. Something of the same kind may be found with the chapter on the Testing and Adulteration of Oils; it is not at all clear from the text that the analysis of a mixture of lubricating oils is of any different nature in the accuracy and certainty of the results of the analysis from the analysis of an ordinary rock or mineral.

On the whole the book is a useful one as a general treatise on the subject. PARKER C. McILHONN.

Wood Pulp and Its Uses. By E. F. CANN, E. J. KERR and R. W. SHAW. 216 pages. 14 illustrations. D. Van Nostrand Company, New York, 1931. Price \$2.00.

The authors have given in this book a general account of the production of the wood pulp industry.

As is to be expected, in covering a field as large as the story of wood pulp, and presenting it both to the technical and general public, certain omissions, as Chapter II, mentioned in part from the "Wastewater in Cellulose," is not technical for the layman. The authors endeavor in the preface that they do not intend the book to be an exhaustive text-book of the subject; this explains why certain other omissions are not more deliberate.

The work is divided into eleven chapters as follows: Chapter I. The Commercial Importance of Wood.

Chapter II. Forest Cellulose as a Chemical Individual and Typical Cellulose. Second. The Lignin-Cumulin, Lignocellulose, Special Chemical Uses in Ammunition and Researches of W. J. Russell.

Chapter III. Wood Pulp in Relation to Sources of Supply, Forest Trees and Forestry.

Chapter IV. The Manufacture of Mechanical Wood Pulp.

Chapter V. Chemical Wood Pulp.

Chapter VI. News and Printings.

Chapter VII. Wood Pulp Bleach.

Chapter VIII. The Utilization of Wood Waste.

Chapter IX. Testing of Wood Pulp for Measure.

Chapter X. Wood Pulp and the Textile Industries.

Chapter XI. Specimen Papers.—Various Types of Paper. This chapter consists of eleven specimen papers of varying composition, giving complete data as to strength, weight, loading, size, etc.

A bibliography has also been included, which gives the character of subject matter of each book. Many of the calculations as to cost, power consumption, statistics, etc., are of course based upon the English system and practice.

The authors have succeeded in producing an instructive book on the numerous uses of wood pulp and waste wood, which is certain to be of interest to the general public and the manufacturers of wood pulp and wood pulp articles. O. KARRS.

NEW PUBLICATIONS.

By D. B. BERGMANN, Librarian American Chemical Society.

Agricultural Chemistry, Yearbook on the Advances in—. By T. BERGMANN. Vol. XIII. L. 8vo., 604 pp. \$3.50. Berlin, 1931. (German.)

Aluminoids, Chemistry of the—. By O. KERNING. 3d Ed. 8vo. \$3.00. F. Vieweg & Sohn, Brunswick. (German.)

Alloys, Composition of the Commoner—. By N. KASER. 1. 8vo., 16 pp. \$0.75. Halle, 1931. (German.)

Analysis, The— and Examination of Agriculturally and Technically Important Substances. By J. KERNIG. 216 Ed. 8vo. \$2.00. Berlin, 1931. (German.)

Analysis, Handbook of Organic—. By H. T. CLARK. 8vo., 202 pp. \$1.25. London, 1931.

Analysis, New Reduction Methods in Volumetric—. By E. KROGER and E. HUBERT. 8vo. \$1.25. New York, 1931.

Analysis, Technical Methods of Chemical—. By GEORGE LEWIS. Vol. II. Translation 8vo., 1104 pp. \$15.75. Clarendon & Jackson, London.

Analysis, The Technical— of Brass and the Non-ferrous Alloys. By W. B. FRAY and R. K. WILSON. 1930., 262 pp. \$2.00. John Wiley & Sons, New York.

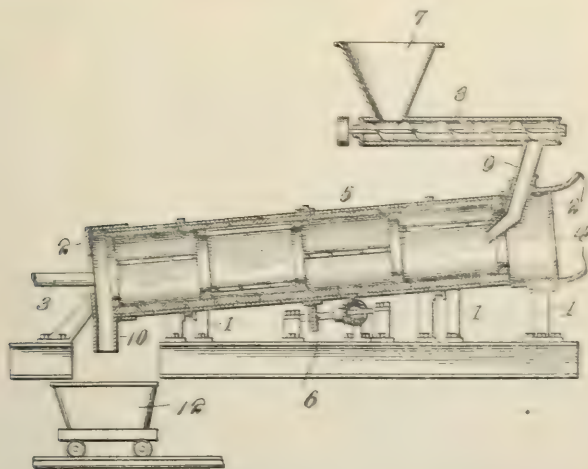
RECENT INVENTIONS.

Reported by C. L. Parker, Senciter of Chemical Physics, Washington, D. C.

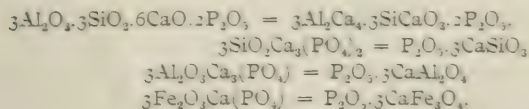
PROCESS OF MAKING PENTOXID OF PHOSPHORUS FROM CALCIUM SILICATE.

U. S. Patent No. 907,086, to S. Peacock, Chicago, assignor to American Cyanamid Company, New York.

A process of making the pentoxid of phosphorus from phosphate rock, or other source of cheap phosphate of lime and silica.



The accompanying illustration shows a type of furnace suitable for carrying out this process. Mixtures of phosphate of lime and silica or silicious clays are proportioned in accordance with the following reactions:



The mixture of phosphate of lime and silica are proportioned in compliance with the reactions suggested, the whole is finely pulverized, mixed and passed through and heated in the furnace to about 1400° C. The phosphorus pentoxid is expelled by volatilization, and is absorbed in water, condensed or used as an acid upon fresh quantities of phosphate rock.

The usefulness of this invention depends upon the production of phosphorus pentoxid free from sulfuric acid, arsenic, antimony, or lower oxids, or phosphorus more or less poisonous or unsuitable for use in plant foods.

PROCESS FOR THE MANUFACTURE OF ASPHALT.

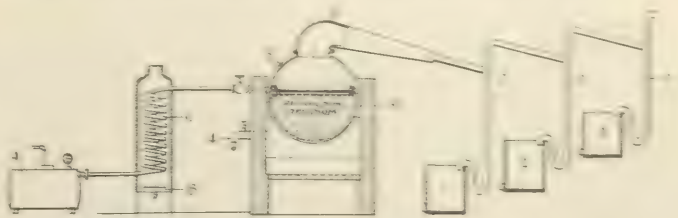
U. S. Patent No. 998,560, to C. B. Forward, Urbana, Ill.

A process for the manufacture of asphalt from petroleum residuum or from crude petroleum from which the lighter oils have been removed.

In handling the crude oil, or residuum, in a commercial way for the production of asphalt, the patentee first tries out a small quantity, about a gallon, in an open vessel at a temperature of about 625° F. The point to be observed is to keep it below the cooking temperature which destroys the value of the resultant product. The lighter oils can be removed much more rapidly in an open vessel than in a closed retort or still.

The patentee proceeds on a commercial scale in the following manner: The petroleum residuum is placed in a retort indicated

by R in the accompanying drawings. It then is subjected to moisture in the tank in B regulated to a temperature of about 175° F. The moisture will precipitate as water and can be drawn off from the bottom of the vessel through an opening C. If there is but a small amount of moisture present, the temperature is put up to 240° to 250° F. and continued. If the temperature rises to 400° or 500° F. before the moisture has been removed, the residuum will foam. After the moisture is drawn off the temperature is increased to 625° F. for a period of 24, 48, or even to hours, according to the gravity of the product. The exact time of subjecting it to the temperature of 625° F.

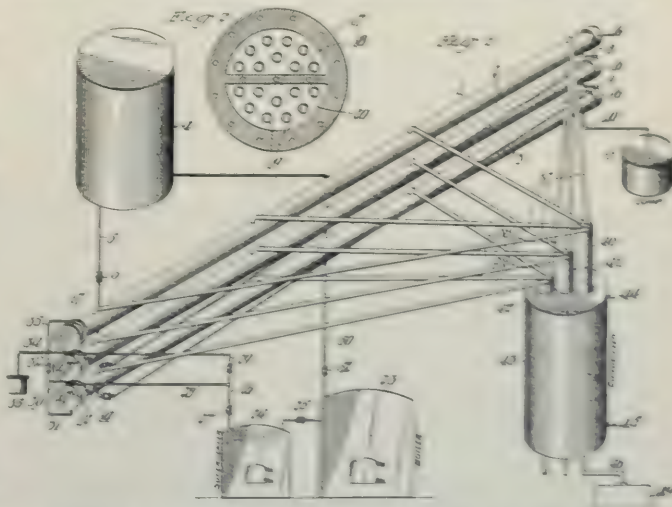


has to be determined in each by experiment with the residuums of different gravities. After 36 to 48 hours at this temperature the resultant material in the retort is tested by withdrawing a small quantity through a suitable opening, as indicated at 5, and checks up at the same time the same quantity of distillate which has been taken off. When the product has acquired the desired consistency the material is transferred to an open vessel, and subjected to a temperature of about 100° F. less than it was in the still, for 5 to 20 hours, according to the product desired.

PROCESS OF REFINING OIL.

U. S. Patent No. 998,837, to Hubert G. Burrows, of Orem,
California.

This invention relates to the treatment of crude oil containing a large amount of mineral matter in suspension, for example, crude oil which is obtained in Santa Barbara county, California.



and which is found to contain mineral matter in the form of infusorial earth, in a state of such fine division that it remains permanently suspended in the oil and cannot be separated therefrom by the usual settling process on account of the viscosity of the oil.

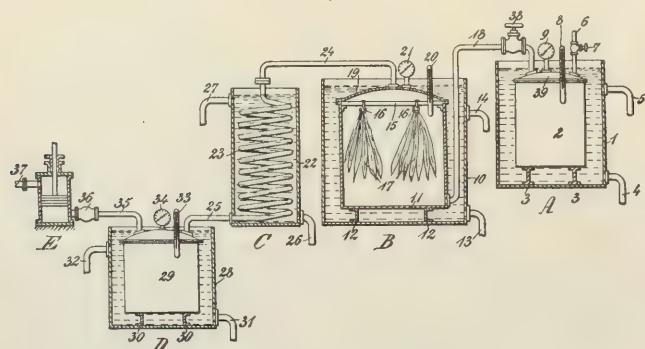
The object of the invention is to provide for effective separation of such mineral matter from the oil. The patentee discovered that by distillation of such oil under proper conditions, finely divided mineral matter will be carried over with the distillate, and, owing to the relatively small viscosity of the distillate, the mineral matter can be separated therefrom by the usual settling operation.

The accompanying illustration shows apparatus in which the process can be advantageously carried out.

METHOD OF REMOVING NICOTIN FROM TOBACCO.

U. S. Patent No. 999,674, to Johannes Sartig, of Nikolassee, near Berlin.

This invention consists in a new method of removing nicotine from tobacco while preserving as much as possible the quality of the tobacco as regards aroma and elasticity, and on the other hand, obtaining the nicotine in its undecomposed state from the tobacco. For attaining this effect, it is necessary to treat the tobacco at as low temperature as possible, and to avoid oxidation of the substances contained therein, so that contamination of the treated tobacco with products of the oxidation of the substances and with so-called resinified matters



is rendered impossible, while at the same time the nicotine removed from the tobacco is recovered in its undecomposed state.

The method consists in treating the tobacco or tobacco products in closed vessels, where the air is rarefied, with low pressure steam at any temperature below 100° centigrade, while simultaneously preventing condensation of the steam in the tobacco by heating the closed vessels from without with surrounding liquid, and in conducting the volatilized nicotine with the steam, carrying it away to devices of any known construction for recovering the nicotine.

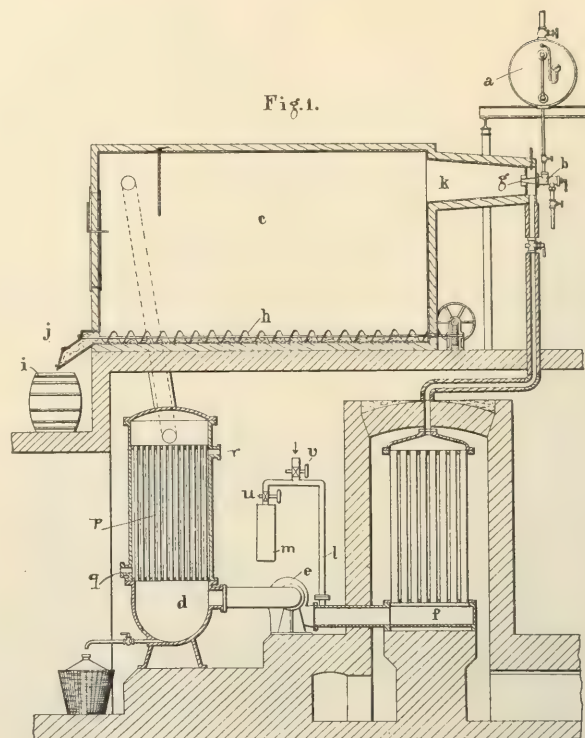
The accompanying illustration shows apparatus in which the process may be carried out.

DESICCATING MILK.

U. S. Patent No. 999,972, to Martin Ekenberg, London. Assignor to Techno-Chemical Laboratories, Limited, of London.

It is known that milk can be desiccated in the form of a fine spray injected into a current of heated air. The product so obtained, however, is oxidized, and the operation involves certain difficulties of a technical nature as a result of using great volumes of air for efficient drying. The patentee has discovered that satisfactory results are obtained if the air be replaced by carbon dioxide or a mixture of carbon dioxide and water vapor.

The invention consists in the use of carbon dioxide, with or without water vapor (in case the latter is used, the proportion of carbon dioxide to the same preferably not exceeding 6 to 1 by volume for the desiccation of milk and milk preparations) as by spraying the liquid or passing it in a finely divided form by, or into a heated current of dry or moist carbon dioxide with



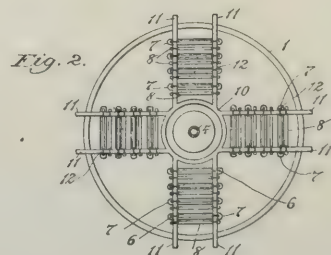
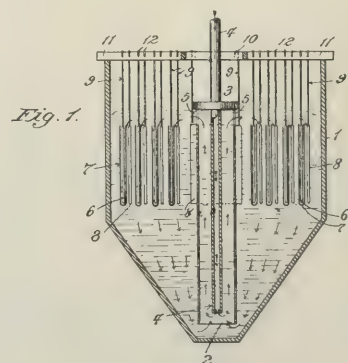
or without added water vapor and then collecting the desiccated product.

The accompanying illustration shows apparatus in which the process can be advantageously carried out.

APPARATUS FOR EXTRACTING METALS FROM THEIR ORES.

U. S. Patent No. 1,001,449, to J. H. Robertson, New York. Assigned to Universal Ore Reduction Company, of Phoenix, Arizona.

This is a method of electrically extracting a metal from a solution containing powdered ore. The continuous circulation of the solution between two conducting surfaces establishes an electrical current which causes the pure metal to be deposited



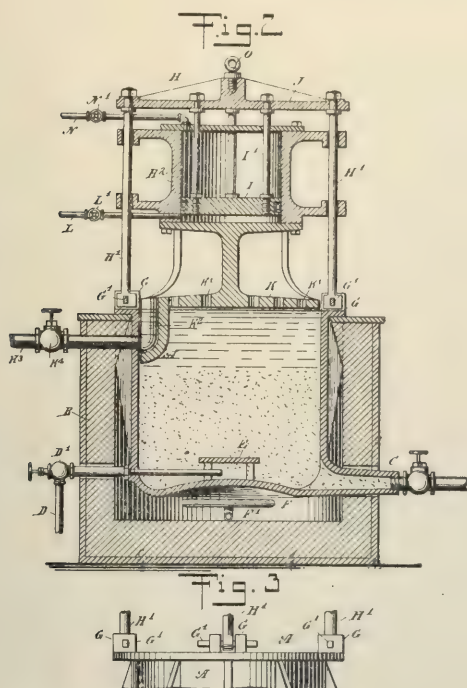
upon one of the surfaces, permitting the tailings to remain in the solution.

The process is carried out by apparatus shown in the accompanying illustration.

PROCESS FOR REFINING AND DESILVERING LEAD.

U. S. Patent No. 1,001,525, to G. P. Hulst, Omaha.

A method of refining and desilverizing impure lead bullion, which consists in melting the impure lead bullion, crystallizing a portion of the lead from the molten bullion by cooling and



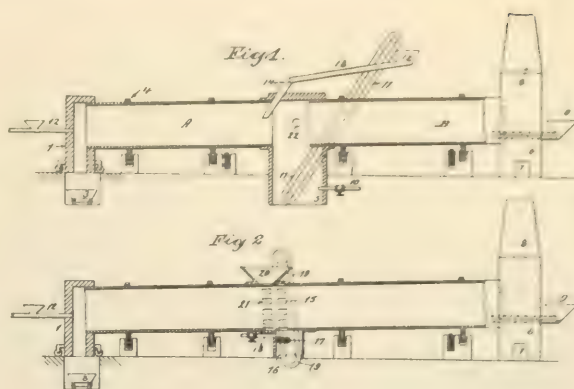
agitation and separating the molten impure lead from the crystallized lead by mechanical pressure applied to the crystals, the impure lead being conducted away from the crystals.

PROCESS OF MAKING CEMENT.

U. S. Patent No. 1,001,582, to Carleton Ellis, of Larchmont, New York. Assignor to Ellis-Foster Company, a Corporation of New Jersey.

This is a process of making cement clinker, which consists in crushing cement raw material to a coarse granular form, calcining the granulated material as a traveling stream, adding to the calcines a quantity of water, sufficient to substantially cool said calcines but insufficient to materially slake them, in regrounding the cooled calcines and clinkering the reground material, said process being conducted throughout in a continuous and non-cumulative manner.

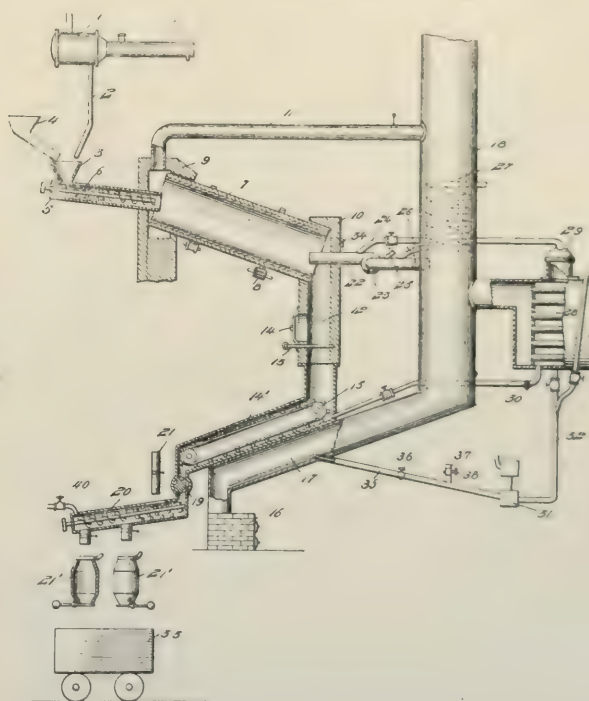
The accompanying illustration shows apparatus in which the process can be carried out.



PROCESS OF MAKING ACETATES.

U. S. Patent No. 1,002,034, to H. O. Chute, Cleveland, and K. P. McElroy, Washington, D. C. Assignors to Ligno-Chemical Company, New York.

This is a method of preparing acetates from products of the digestion of woody fibers with alkali by heating such products under regulated conditions, and in recovering both the acetate formed, and the excess of alkaline reagent.



An alkali solution is produced, consisting of woody fiber constituents, the same being absorbed by a material capable of doing so. The mass is oxidized while in a heated state by diluted air, carbonizing by a higher heat out of contact with air, and separating the carbonate and acetate of alkali from the carbonized mass.

MARKET REPORT.

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR MONTH OF NOVEMBER.)

Full List of Weekly Quotations, see "Oil, Paint & Drug Reporter."

ORGANIC CHEMICALS.

Acetanilid.....Lb.	20 1/2 @	23
Acetone (drums).....Lb.	13 3/4 @	15
Alcohol, grain (188 proof).....Gal.	2.56 @	2.58
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	3.00 @	3.25
Acetic Acid.....C.	1.87 1/2 @	2.02 1/2
Aniline Oil.....Lb.	10 3/4 @	11 1/2
Benzoic Acid.....Oz.	11 1/4 @	12
Carbon Tetrachloride (drums).....Lb.	7 3/4 @	8 1/4
Carbon Bisulphide.....Lb.	5 @	7
Chloroform.....Lb.	27 @	33
Carbolic Acid (drums).....Lb.	17 @	18 2/3
Citric Acid (domestic).....Lb.	38 1/2 @	39
Camphor (refined in bulk).....Lb.		44 1/2
Dextrine (imported potato).....Lb.	6 1/4 @	7 1/4
Dextrine (corn).....C.	2.87 @	3.03
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....Lb.	19 1/2 @	20
Iodoform.....Lb.	2.95 @	3.00
Oxalic Acid.....C.	7 1/4 @	7 1/2
Pyrogalllic Acid (bulk).....Lb.	1.25 @	1.55
Salicylic Acid.....Lb.	32 @	34
Starch (corn).....C.	2.15 @	2.30
Starch (potato).....Lb.	5 1/4 @	5 1/2
Starch (rice).....Lb.	7 @	8
Starch (wheat).....Lb.	4 7/8 @	5 1/4
Tannic Acid (regular in bulk).....Lb.	58 @	60
Tartaric Acid, crystals.....Lb.	30 1/4 @	30 3/4

INORGANIC CHEMICALS.

Acetate of Lime (gray).....C.	2.00 @	2.05
Acetate of Lead (brown, broken).....Lb.	7 3/4 @	8
Alum (lump).....C.	1.75 @	2.00
Ammonium Carbonate, domestic.....Lb.	8 @	8 3/4
Ammonium Chloride, gray.....Lb.	6 @	6 1/4
Aluminum Sulphate.....Lb.	90 @	1 3/4
Ammonium Vanadate.....Oz.	41 @	50
Aqua Ammonia (drums) 16°.....Lb.	2 1/2 @	2 1/2
Arsenic, white.....Lb.	2 3/8 @	2 5/8
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chlorate.....Lb.	15 @	17
Barium Chloride.....C.	1.90 @	2 1/4
Barium Nitrate.....Lb.	5 1/2 @	6 1/4
Borax, crystals (bags).....Lb.	3 1/2 @	4
Boric Acid, crystals.....Lb.	7 @	7 1/2
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.30 @	1.35
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	4 1/2 @	4 3/4
Calcium Chloride.....C.	65 @	90
Calomel, American.....Lb.	94 @	96
Chalk (light precipitated).....Lb.	4 1/2 @	6
Cobalt Oxide.....Lb.	80 @	1.00
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	8.00 @	12.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (bags).....C.	60 @	85
Hydrochloric Acid (18°).....C.	1.15 @	1.55
Hydrochloric Acid (22°).....C.	1.45 @	1.75
Iodine (resublimed).....Lb.	2.60 @	2.65
Lead Nitrate.....Lb.	8 @	8 5/8
Lithium Carbonate.....Lb.	57 @	60
Magnesite (raw).....Ton	10.00 @	11.00
Mercuric Chloride.....Lb.	85 @	88
Nitric Acid, 36°.....Lb.	3 5/8 @	4 1/2
Nitric Acid, 42°.....Lb.	4 7/8 @	5 1/4

Phosphorus.....Lb.	45 @	1.00
Phosphoric Acid, s. g. 1.75.....Lb.	21 @	25
Plaster of Paris.....C.	1.50 @	1.70
Potassium Bromide.....Lb.	31 @	34
Potassium Permanganate (bulk).....Lb.	9 3/8 @	10 3/4
Potassium Cyanide (bulk).....Lb.	20 @	24
Potassium Iodide (bulk).....Lb.	2.10 @	2.15
Potassium Chlorate, crystals.....Lb.	8 1/4 @	9 1/2
Potassium Nitrate (crude).....Lb.	4 7/8 @	4 7/8
Potassium Bichromate, 50°.....Lb.	7 3/8 @	7 3/4
Pumice Stone.....Lb.	2 @	4
Quicksilver.....Lb.	63 1/2 @	65 1/2
Salt Cake (glass-makers).....C.	55 @	65
Silver Nitrate.....Oz.	34 @	36
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 @	4 1/2
Sodium Chlorate.....Lb.	8 1/4 @	9 1/2
Sodium Bicarbonate (English).....Lb.	2 3/4 @	3
Sodium Bichromate.....Lb.	5 5/8 @	5 2/4
Sodium Bisulfite (not incl. pkg.).....C.	75 @	1.37 1/2
Sodium Hydroxide, 60 per cent.....C.	1.80 @	1.85
Sodium Hyposulfite.....C.	1.30 @	1.50
Sodium Nitrate, 95 per cent., spot... C.	2.22 1/2 @	2.25
Sodium Silicate (liquid).....C.	65 @	1.50
Sodium Stannate.....Lb.	9 3/4 @	10
Strontium Nitrate.....Lb.	7 1/4 @	8
Sulphur, Roll.....C.	1.85 @	2.15
Sulphur, Flowers.....C.	2.20 @	2.60
Sulphuric Acid, 60° B.....C.	85 @	1.00
Talc (American).....Ton	15.00 @	20.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	12 @	12
Tin Oxide.....Lb.	45 @	47
Tin Chloride (36°).....Lb.	11 @	11 1/2
Zinc Chloride (granulated).....Lb.	4 1/2 @	4 1/2
Zinc Sulphate.....Lb.	2 1/4 @	2 1/2

OILS, WAXES, ETC.

Beeswax (pure white).....Lb.	40 @	45
Black Mineral Oil, 29 Gravity.....Gal.	12 @	12 1/2
Castor Oil (No. 3).....Lb.	10 @	11
Ceresin (yellow).....Lb.	9 @	20
Corn Oil.....C.	6.30 @	6.35
Cottonseed Oil (crude), f. o. b. mill...Gal.	33 @	33 1/2
Cylinder Oil (light, filtered).....Gal.	19 1/2 @	20
Japan Wax.....Lb.	8 1/2 @	8 3/4
Lard Oil (prime winter).....Gal.	82 @	85
Linseed Oil (double-boiled).....Gal.	87 @	88
Paraffine Oil (high viscosity).....Gal.	23 1/2 @	24
Paraffine (crude 120 @ 122 m. p.).....Lb.	3 @	3 1/8
Rosin Oil (first run).....Gal.	36 @	50
Spindle Oil, No. 1.....Gal.	14 @	14 1/2
Sperm Oil (bleached winter) 38°.....Gal.	76 @	78
Stearic Acid (double-pressed).....Lb.	10 1/4 @	10 1/2
Tallow (acidless).....Gal.	63 @	65
Tar Oil (distilled).....Gal.	30 @	31

METALS.

Aluminum [No. 1 ingots].....Lb.	18 1/2 @	19
Antimony (Hallet's).....Lb.	7.50 @	7.85
Bismuth (London).....Lb.	— @	1.80
Copper (electrolytic).....Lb.	12.25 @	12.35
Copper (lake).....Lb.	12 1/2 @	12 5/8
Lead, N. Y.....Lb.	4.20 @	4.25
Nickel.....Lb.	40 @	50
Platinum (refined).....Oz.	48.50 @	49.00
Silver.....Oz.	54 @	55
Tin.....Lb.	— @	42
Zinc.....Lb.	6.15 @	6.25

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